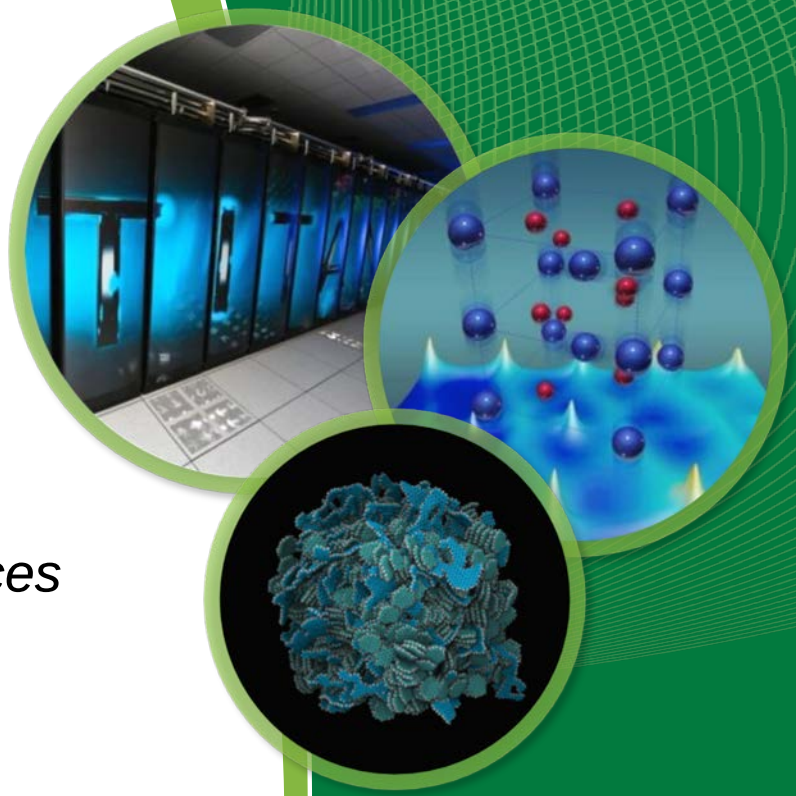
Maximizing Current Density for Electrochemical Conversion of Flue Gas CO_2 to Ethanol



Adam Rondinone

Center for Nanophase Materials Sciences

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NETL/DOE Field Work Proposal #FEAA132

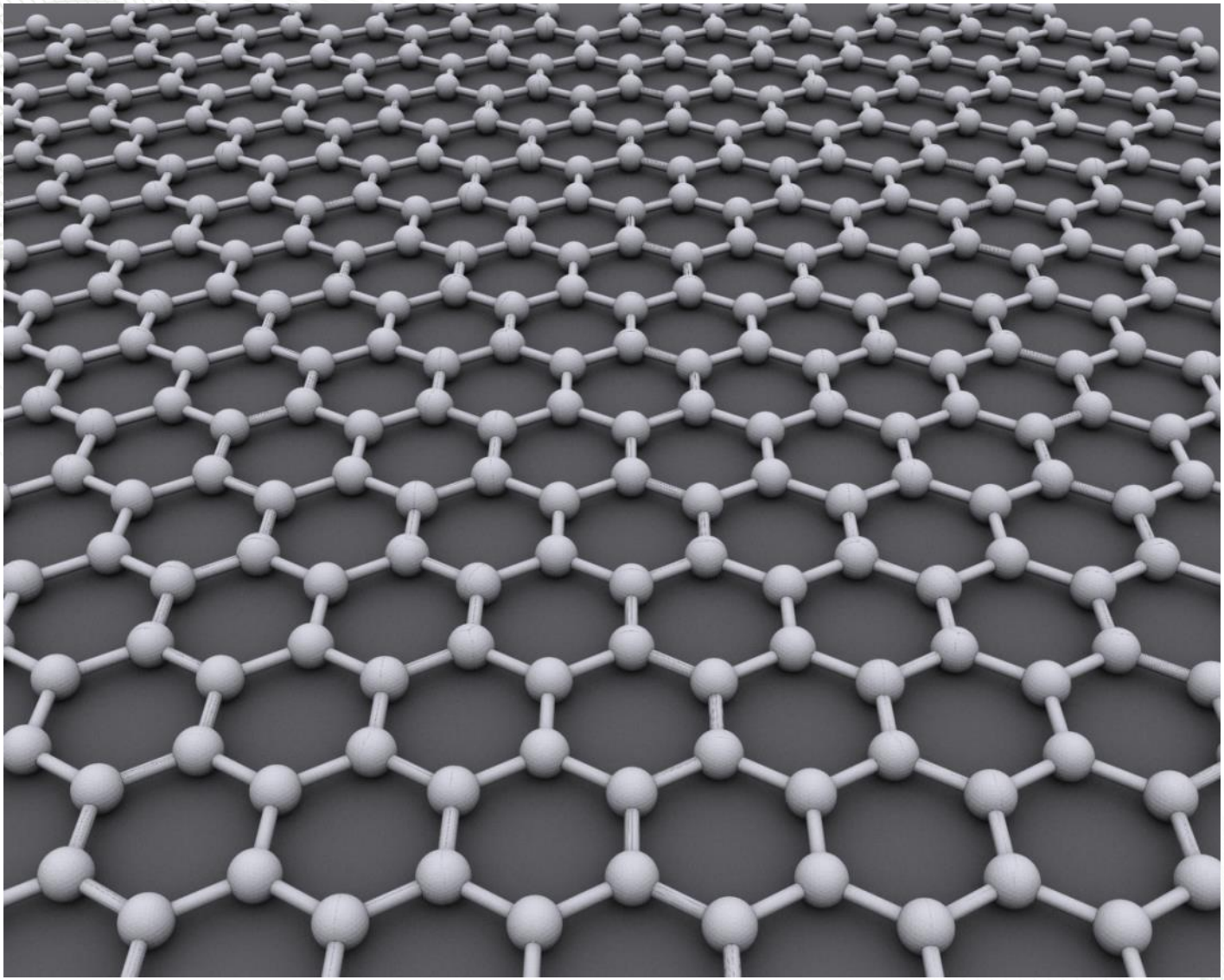
NETL/DOE Project Manager Sai Gollakota

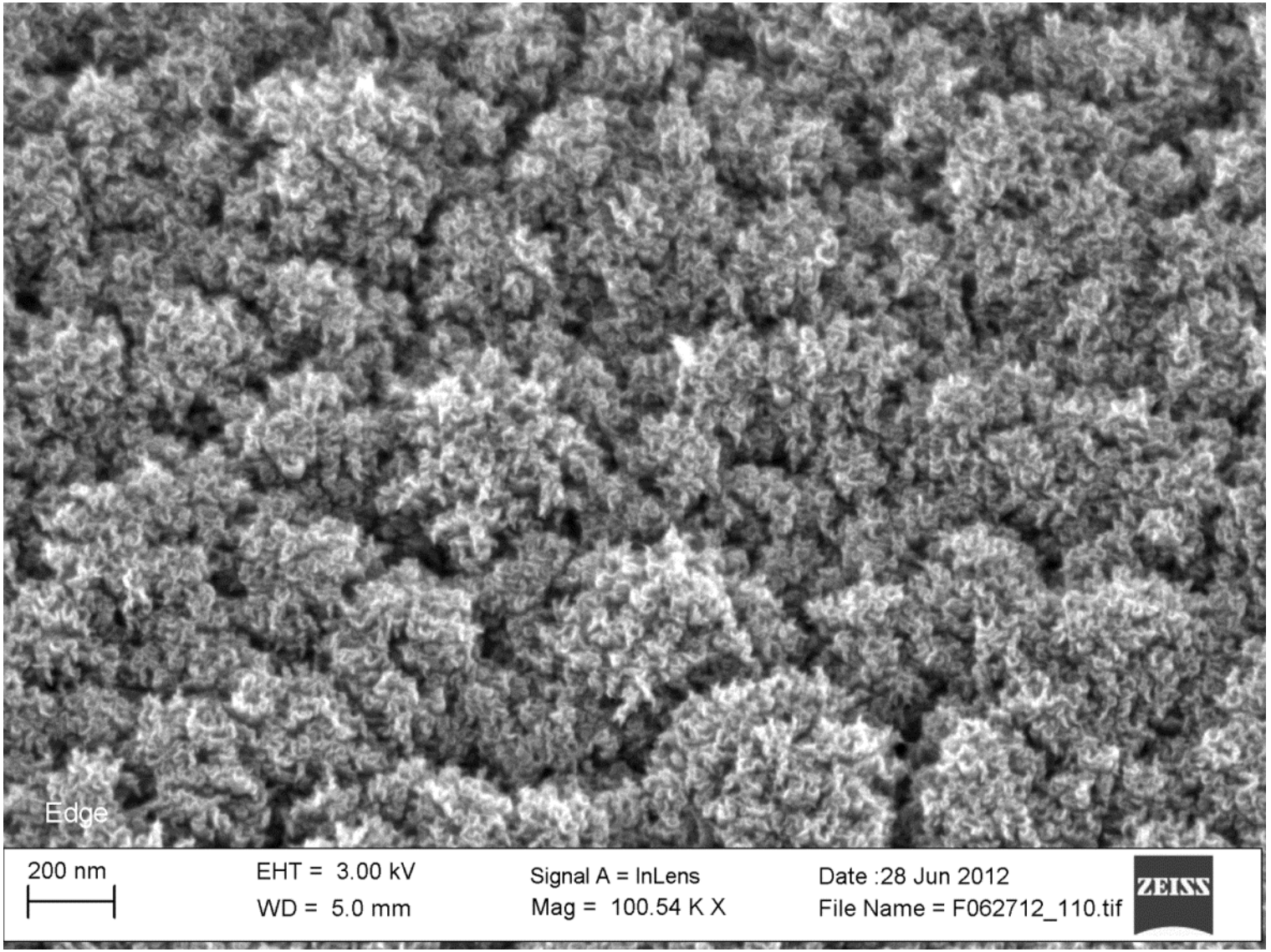
Project Final Meeting at NETL: 18 July 2018

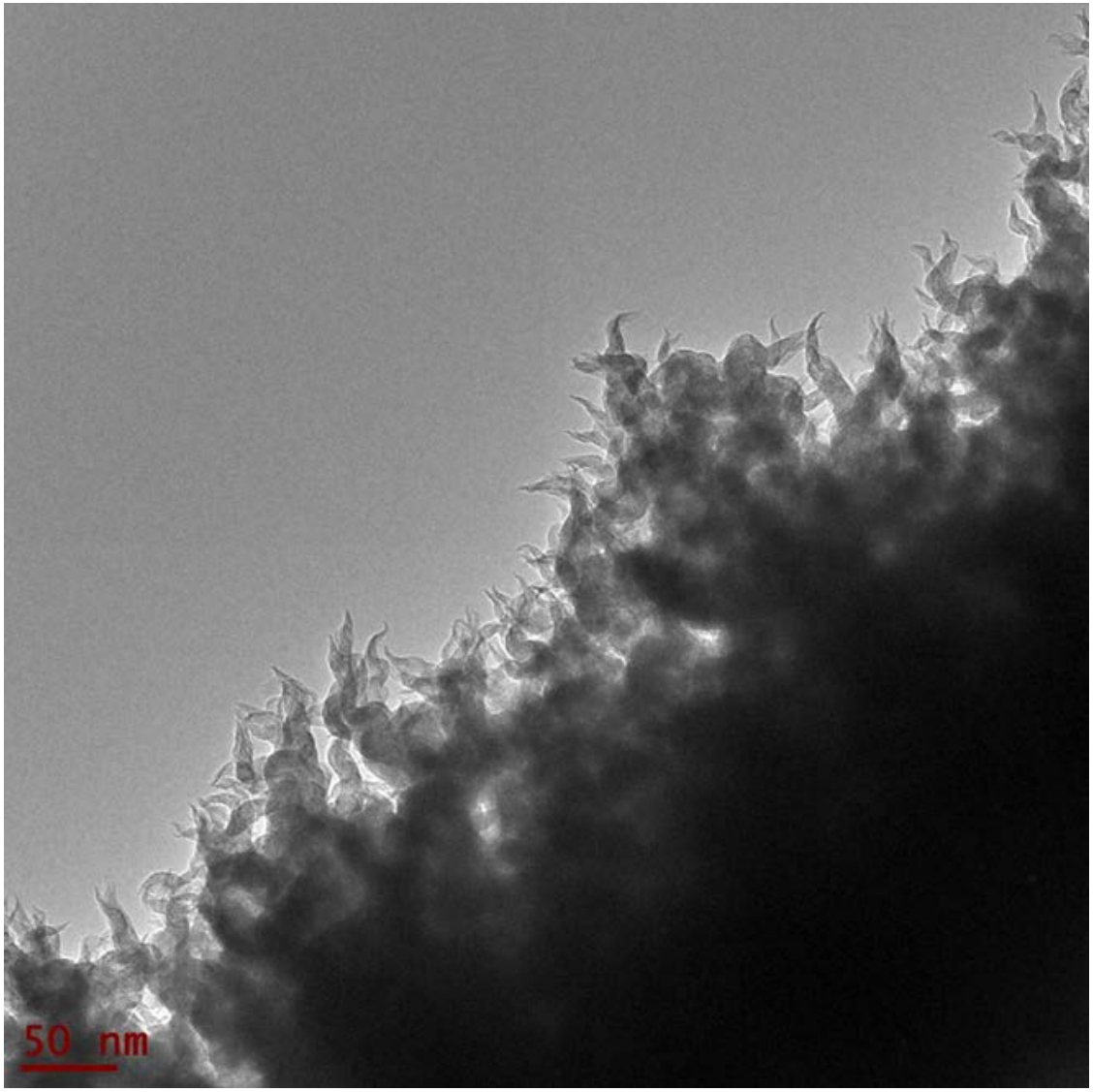
Outline

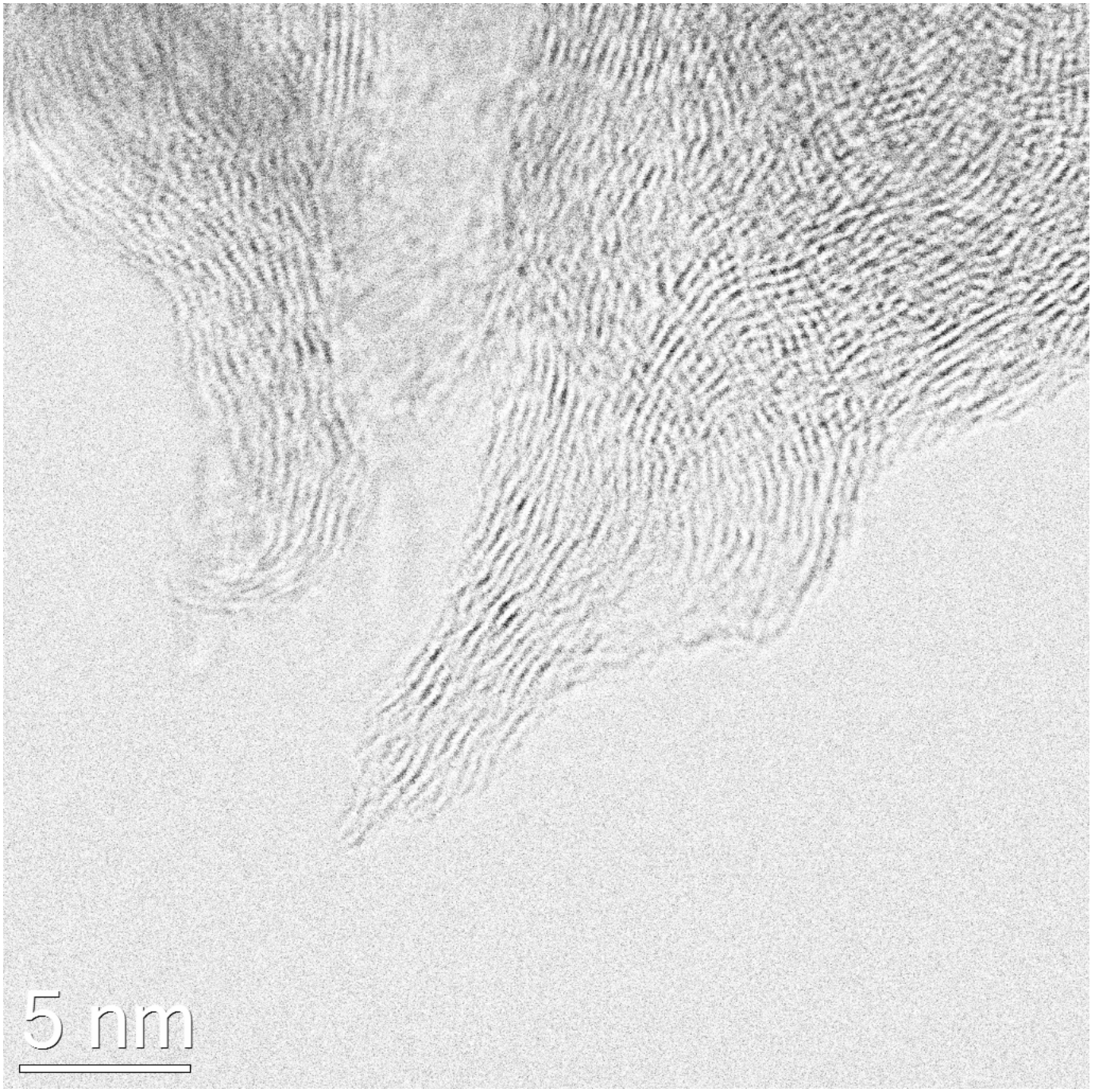
- Carbon Nanospikes and CO_2 Electrochemistry
  - Motivation
  - Mechanism of Reaction
- Fossil Energy Project
  - Objectives
  - Results

Graphene: Single Layer, Hexagonal Carbon

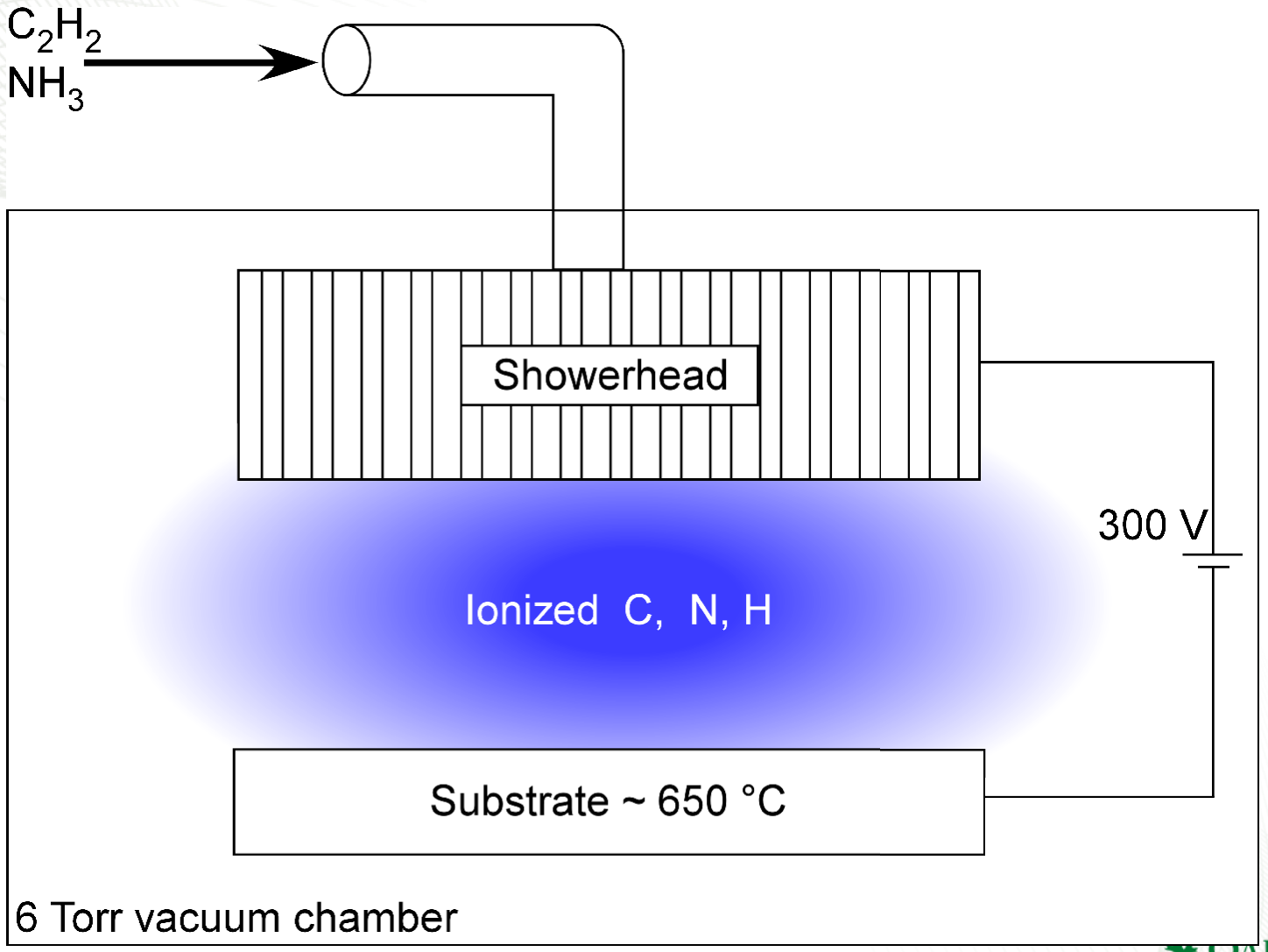



Edge
200 nm
EHT = 3.00 kV
WD = 5.0 mm
Signal A = InLens
Mag = 100.54 K X
Date :28 Jun 2012
File Name = F062712_110.tif
ZEISS

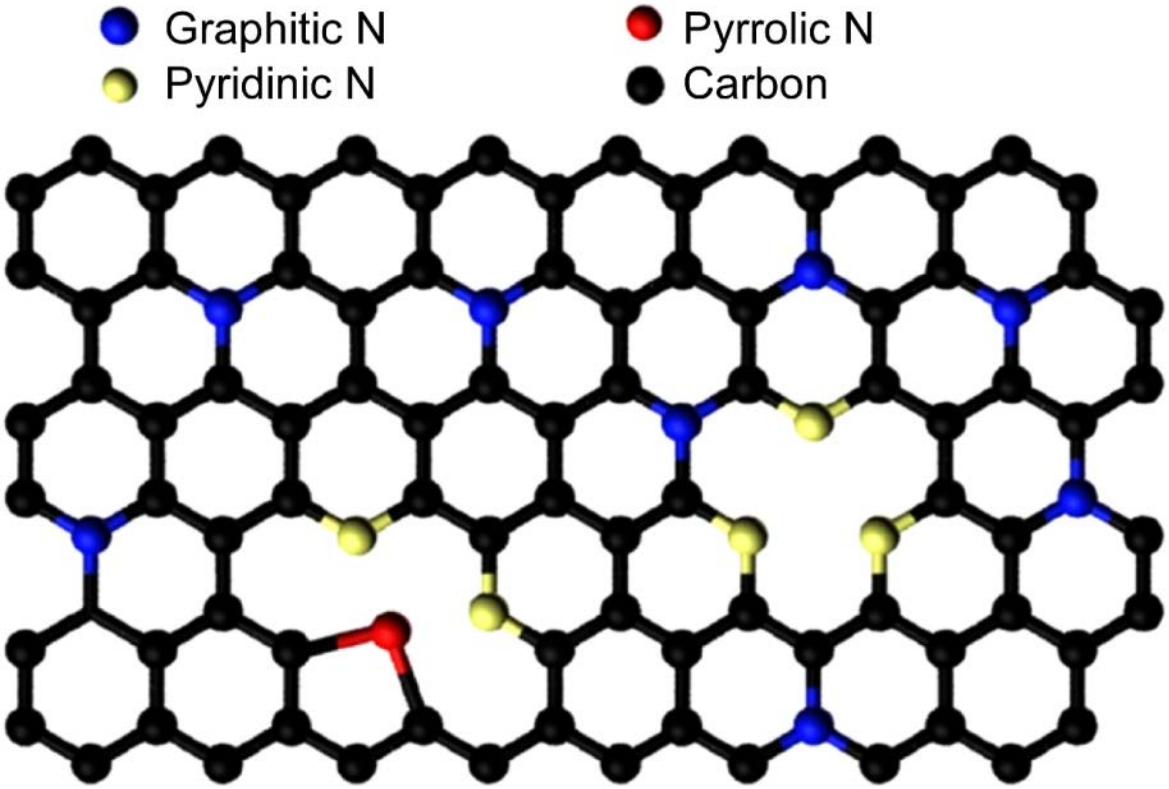

50 nm


5 nm

Plasma-Enhanced Chemical Vapor Deposition (PECVD)



5% Nitrogen Doping

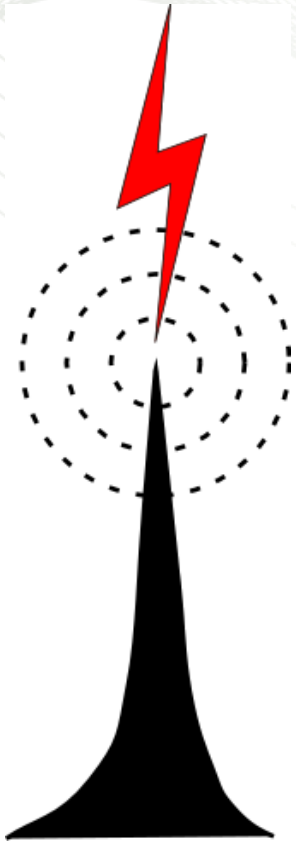


- Pyrolysis elemental analysis: N doping (5.1 ± 0.2 %)
- XPS: N 1s
  - pyridinic (~25%),
  - pyrrolic (~19%),
  - graphitic (~55%).

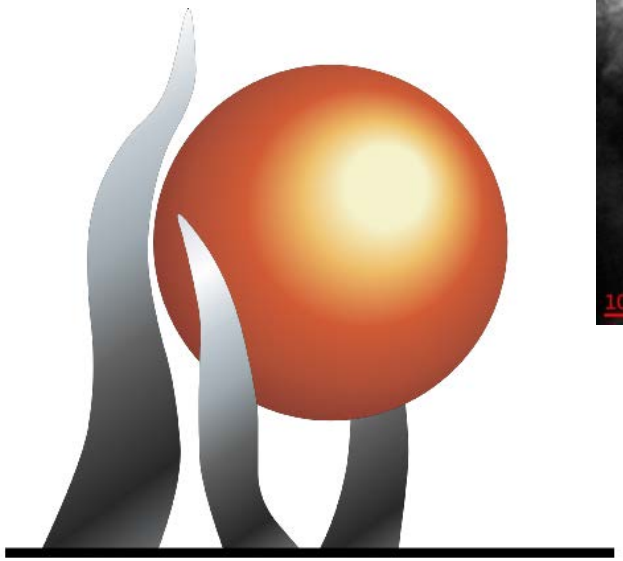
Cho, Hyunjin, et al. "Catalyst and doping methods for arc graphene." Nanotechnology 25.44 (2014): 445601.

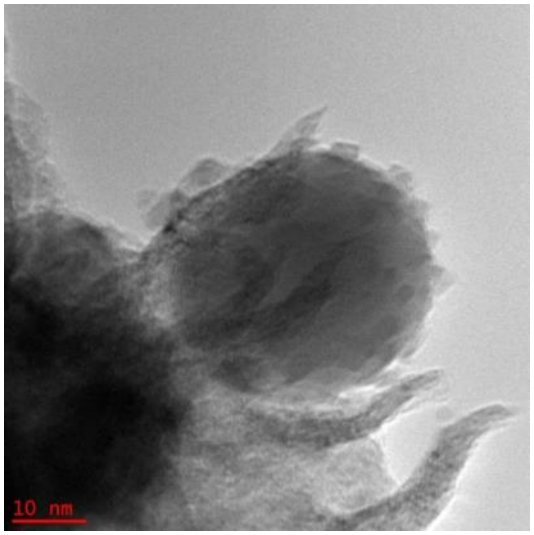
Carbon Nanospikes are Dense and Numerous

- Approximately $1x10^{13}$ spikes per sheet of copy paper
- Each nanospike will concentrate electric field



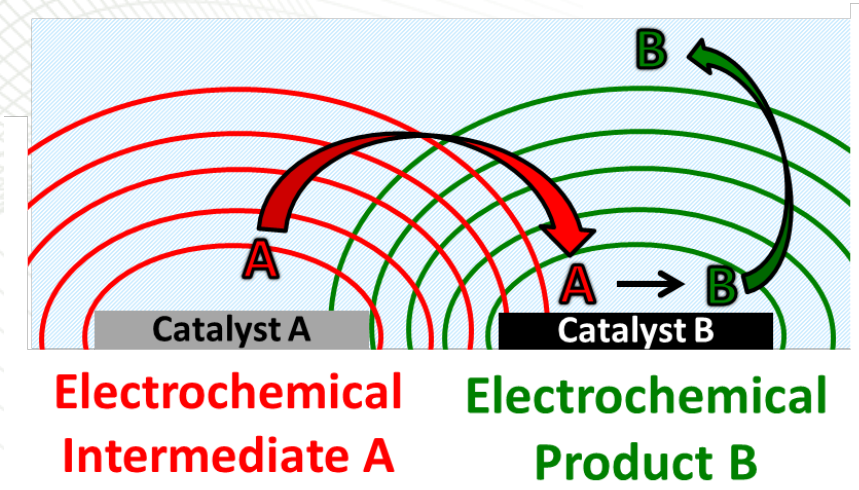
Copper Salt





CO_2 Electroreduction

- Motivation: explore sequential electrocatalysis

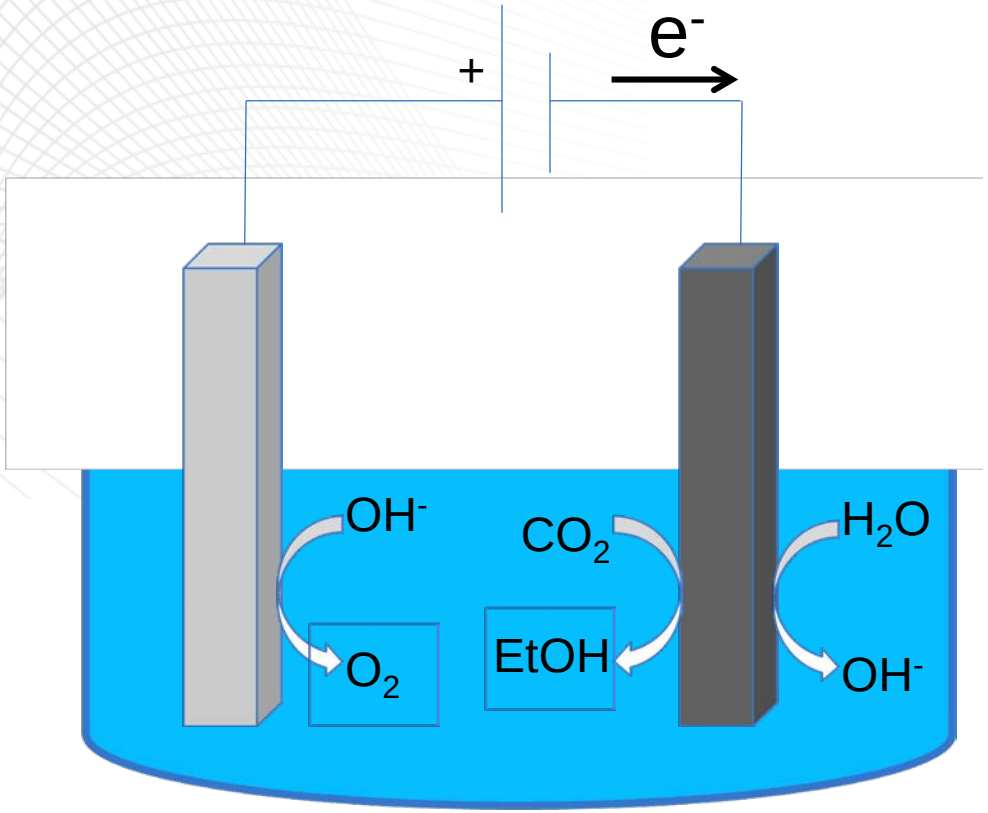


Can engineered, nanoscale electrocatalysts control the activity and/or selectivity?

Needed a multi-electron test case: CO_2

- Copious literature on copper electrodes for CO_2
  - Nanostructured copper on glassy carbon: CH_4
  - Textured copper film: CO to ethanol
  - Bulk copper plates: mixture of hydrocarbons depending on electrolyte

Electrolysis ~ Charging a Battery



CABB Group GmbH

Cathode (catalyst) half-reaction: $9H_2O + 9e^- \rightarrow 9H + 9OH^-$

$2CO_2 + 9H + 3e^- \rightarrow C_2H_5OH + 3OH^-$

Anode half-reaction: $12OH^- \rightarrow 3O_2 + 6H_2O + 12e^-$

Literature Indicates Diverse Product Mix

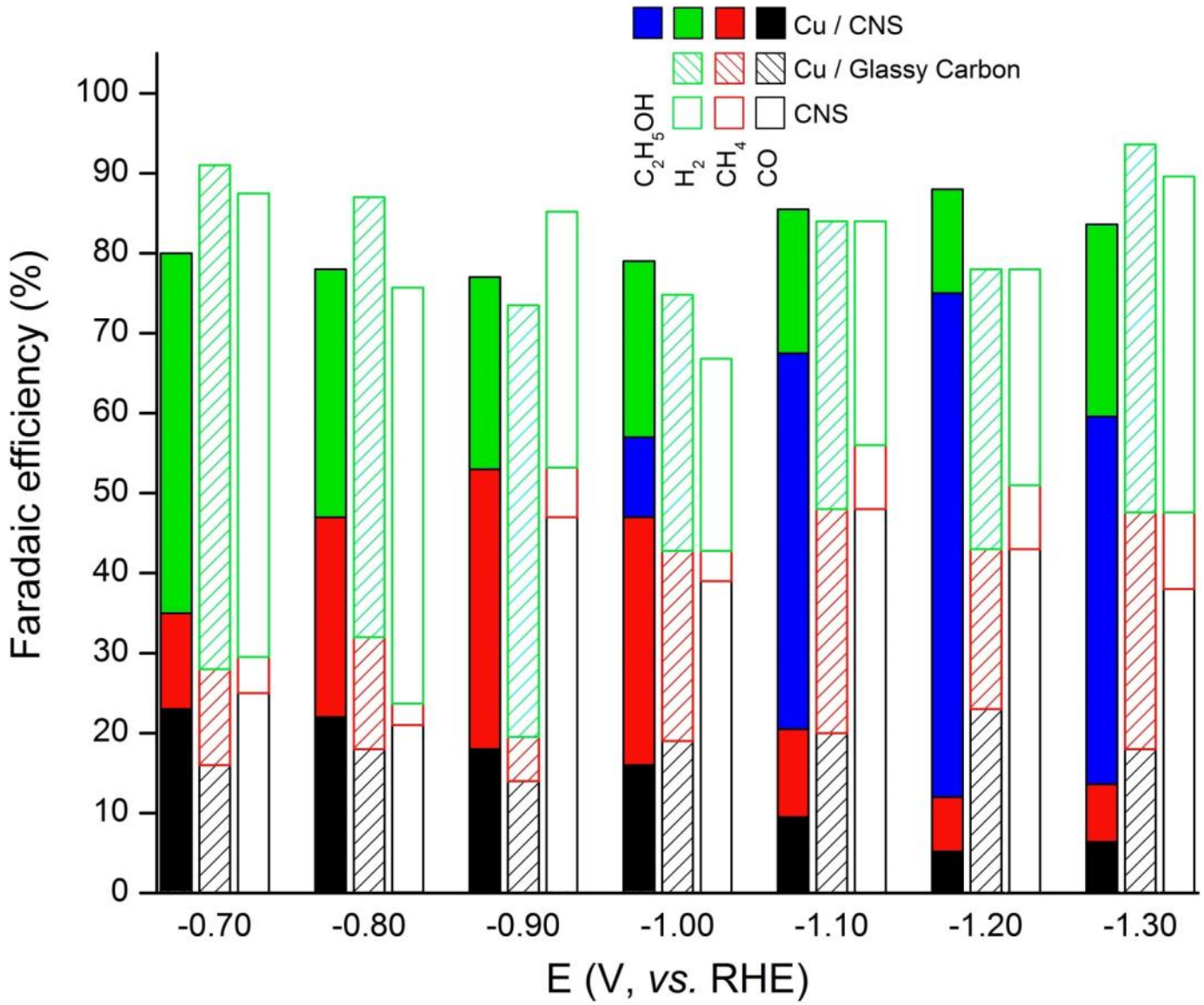
Table 1. Faradaic efficiencies of products from the electroreduction of CO_2 at a Cu electrode at 5 mA cm^{-2} in various solutions at 19 °C

electrolyte	conc. /mol dm^{-3}	pH[a]	potential /V *vs.*NHE	Faradaic efficiency (%) CH_4	C_2H_4	EtOH	Pr^nOH	CO	$HCOO^-$	H_2	total
$KHCO_3$	0.1	6.8	−1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0
KCl	0.1	5.9	−1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
	0.5		−1.39	14.5	38.2	[b]	[b]	3.0	17.9	12.5	
$KClO_4$	0.1	5.9	−1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K_2SO_4	0.1	5.8	−1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K_2HPO_4	0.1	6.5	−1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5
	0.5	7.0	−1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7

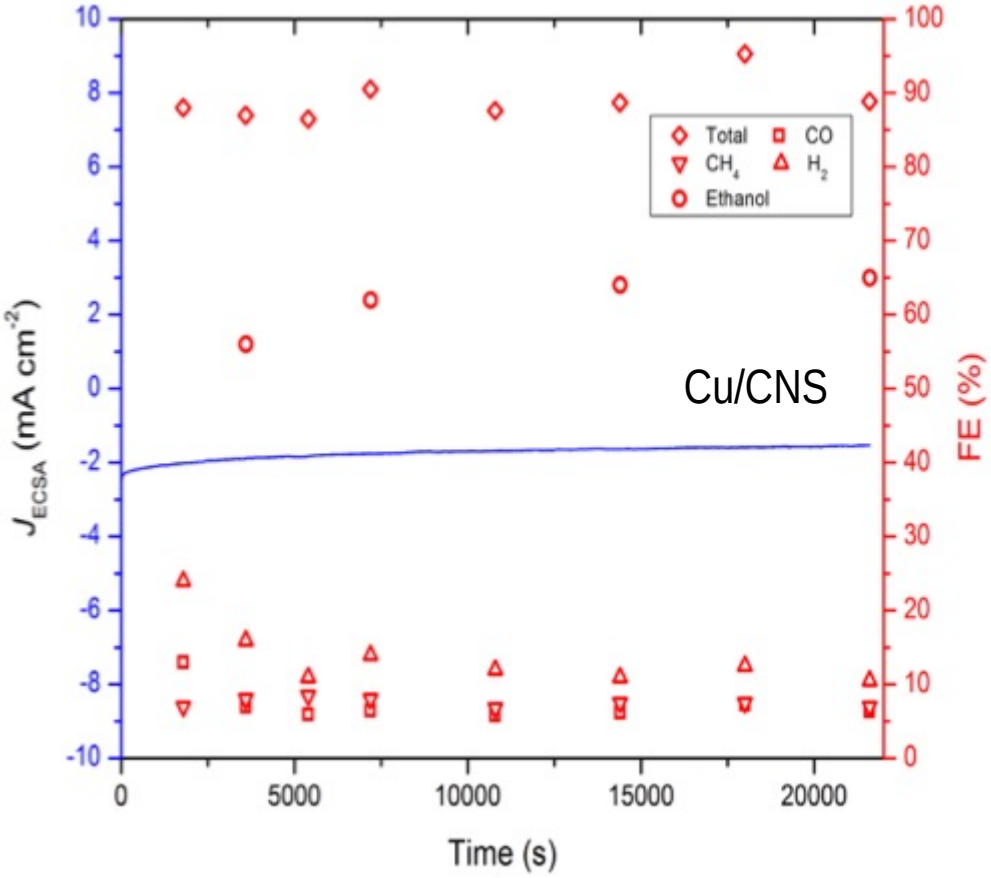
[a] pH values were measured for bulk solutions after electrolyses. [b] Not analysed.

J. Chem. Soc., Faraday Trans. 1, 1989, **85**(8), 2309–2326

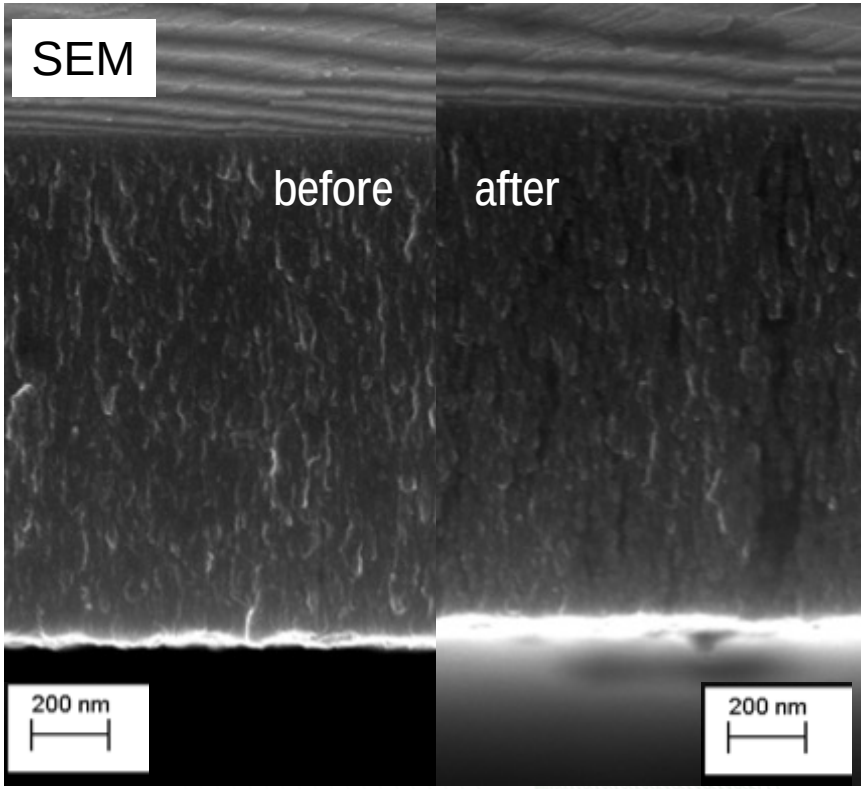
Result: Products from CO_2 Reduction



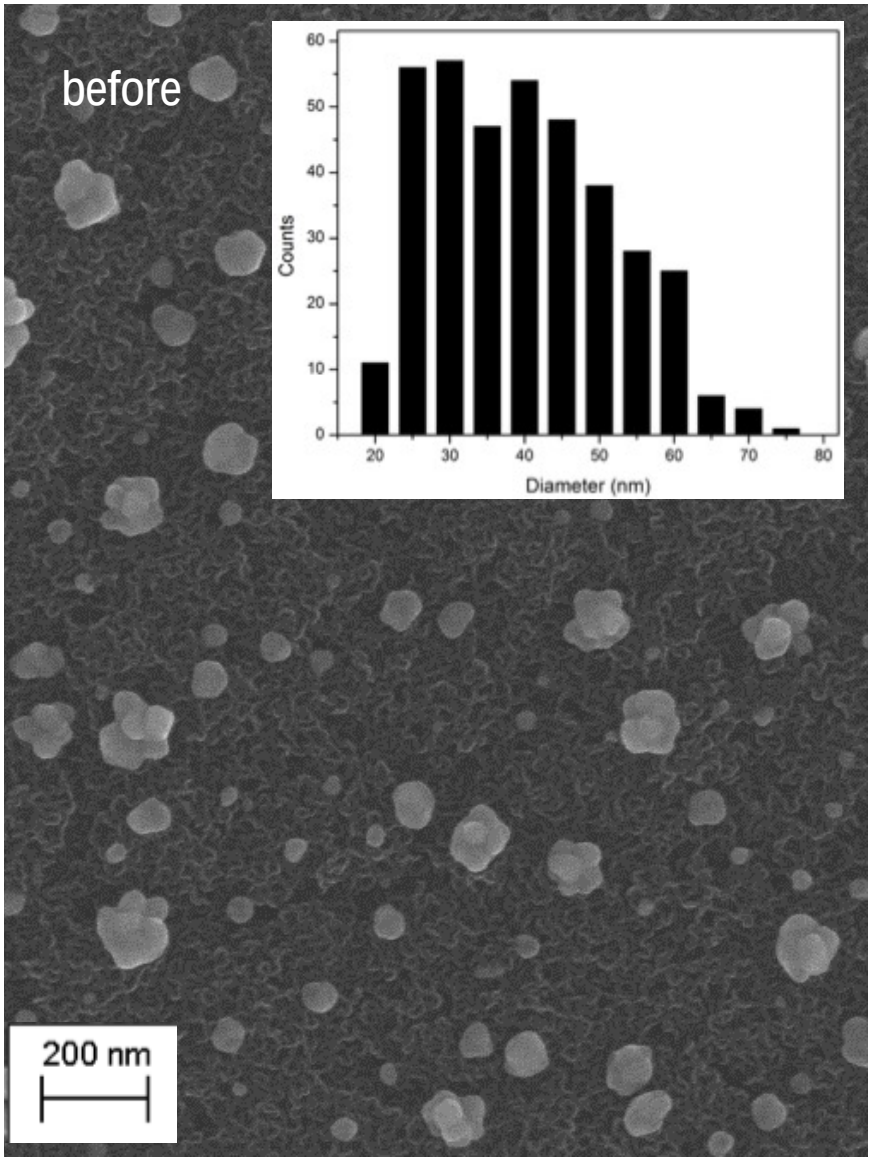
Stability

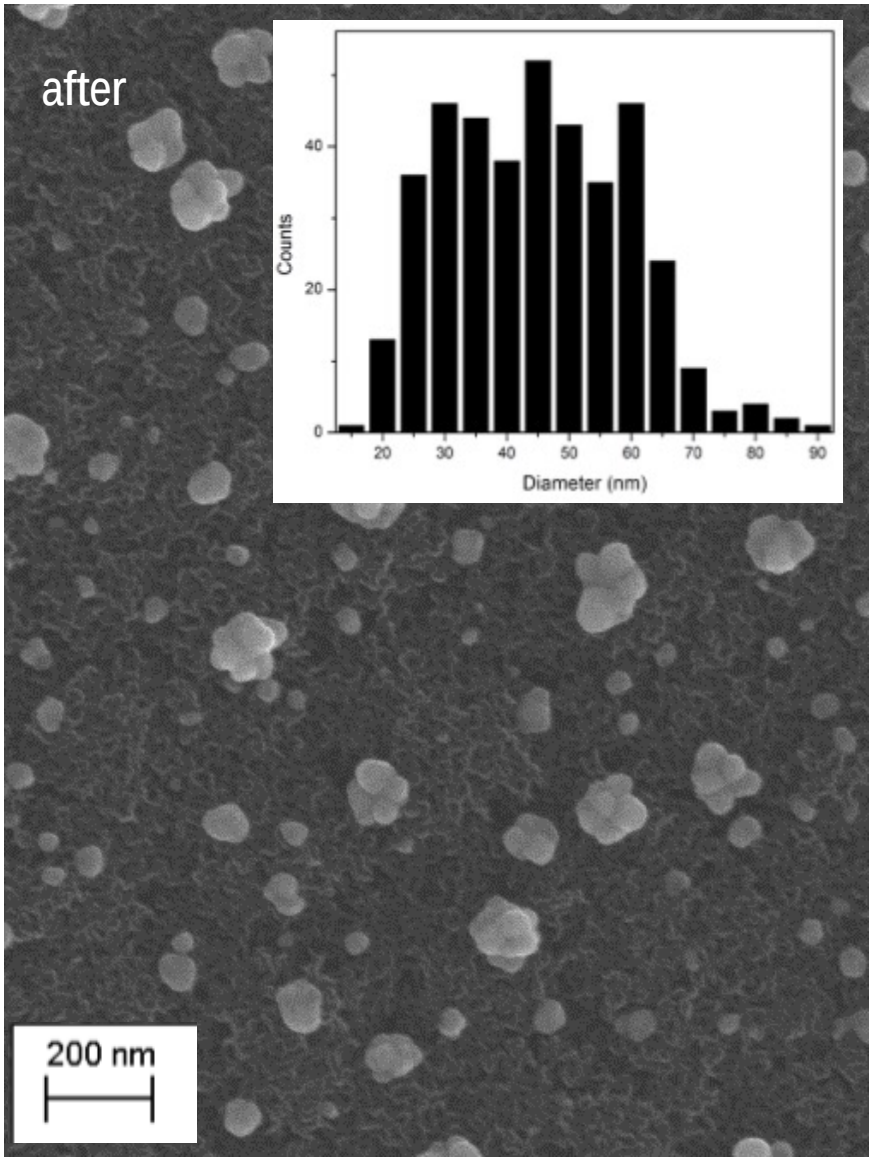


- Stable over a 6-hour experiment.
- Full formation rate for major products achieved in 1 hour.

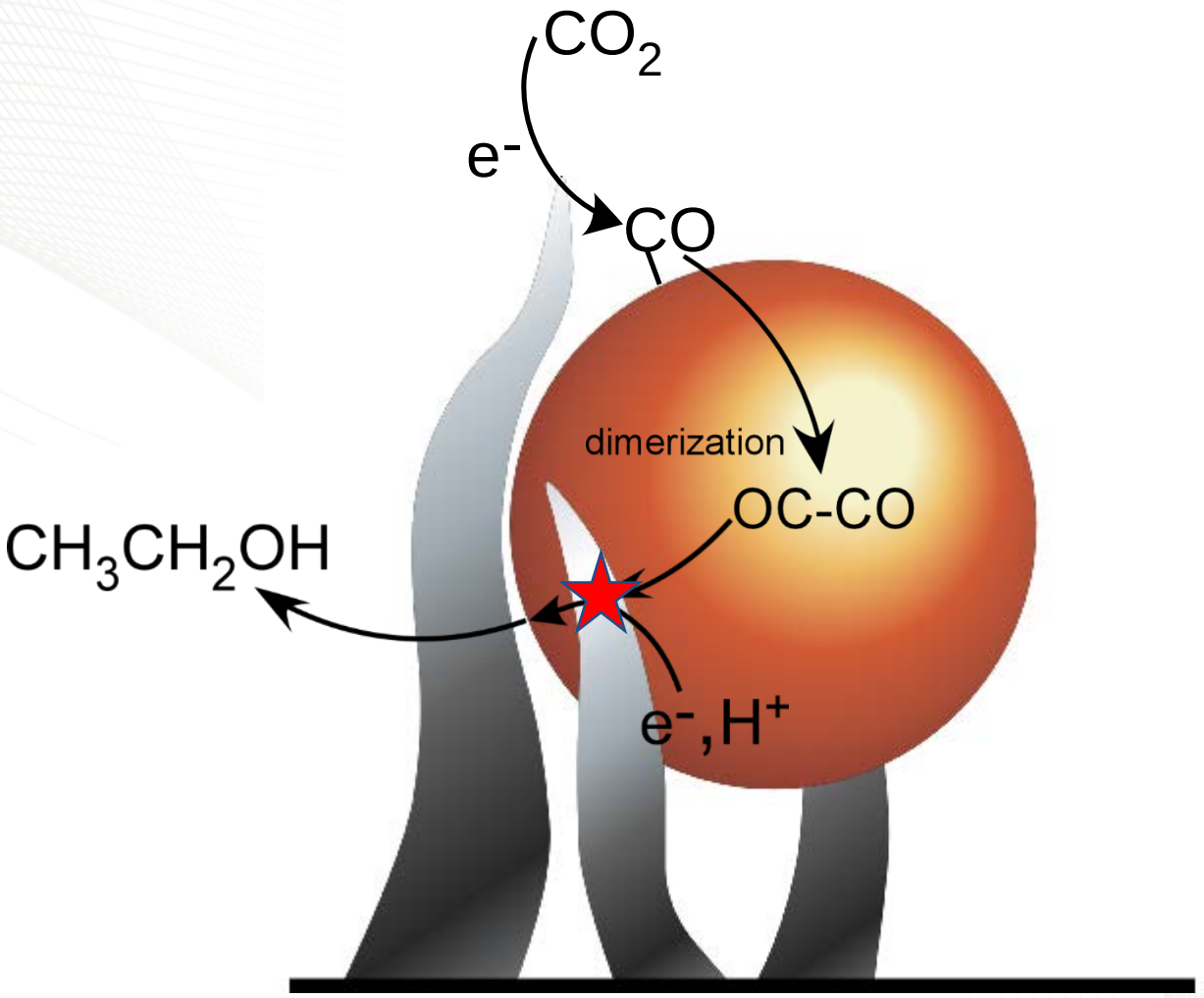


- Side-view SEM images show no change in CNS thickness


before
Counts
Diameter (nm)
0
10
20
30
40
50
60
20
30
40
50
60
70
80
200 nm


after
Counts
Diameter (nm)
0
20
40
20
30
40
50
60
70
80
90
200 nm

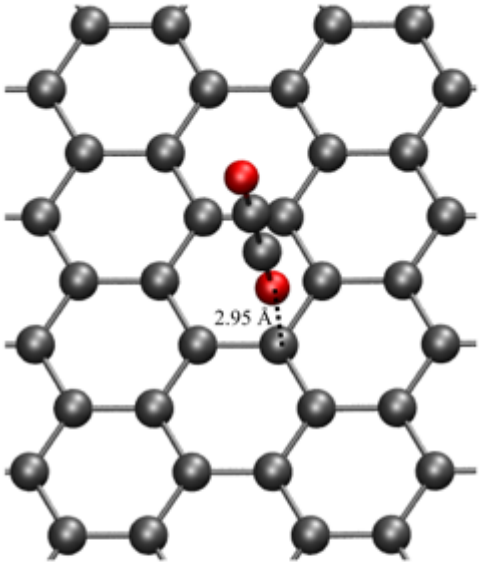
Hypothetical Mechanism



Mechanism

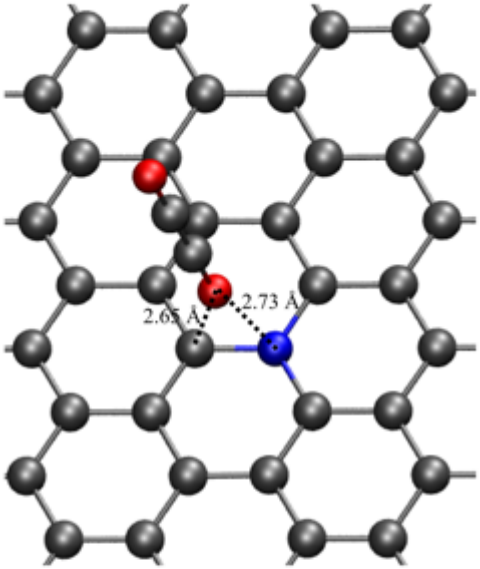
(a) pristine and flat graphene

Binding energy: 0.19 eV



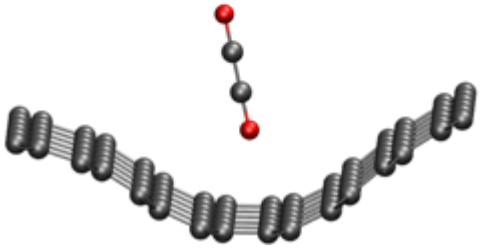
(b) N-doped and flat graphene

Binding energy: 0.64 eV



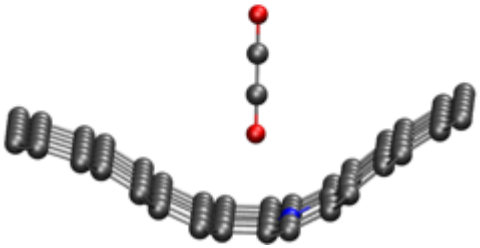
(c) pristine and curved graphene

Binding energy: 0.34 eV



(d) N-doped and curved graphene

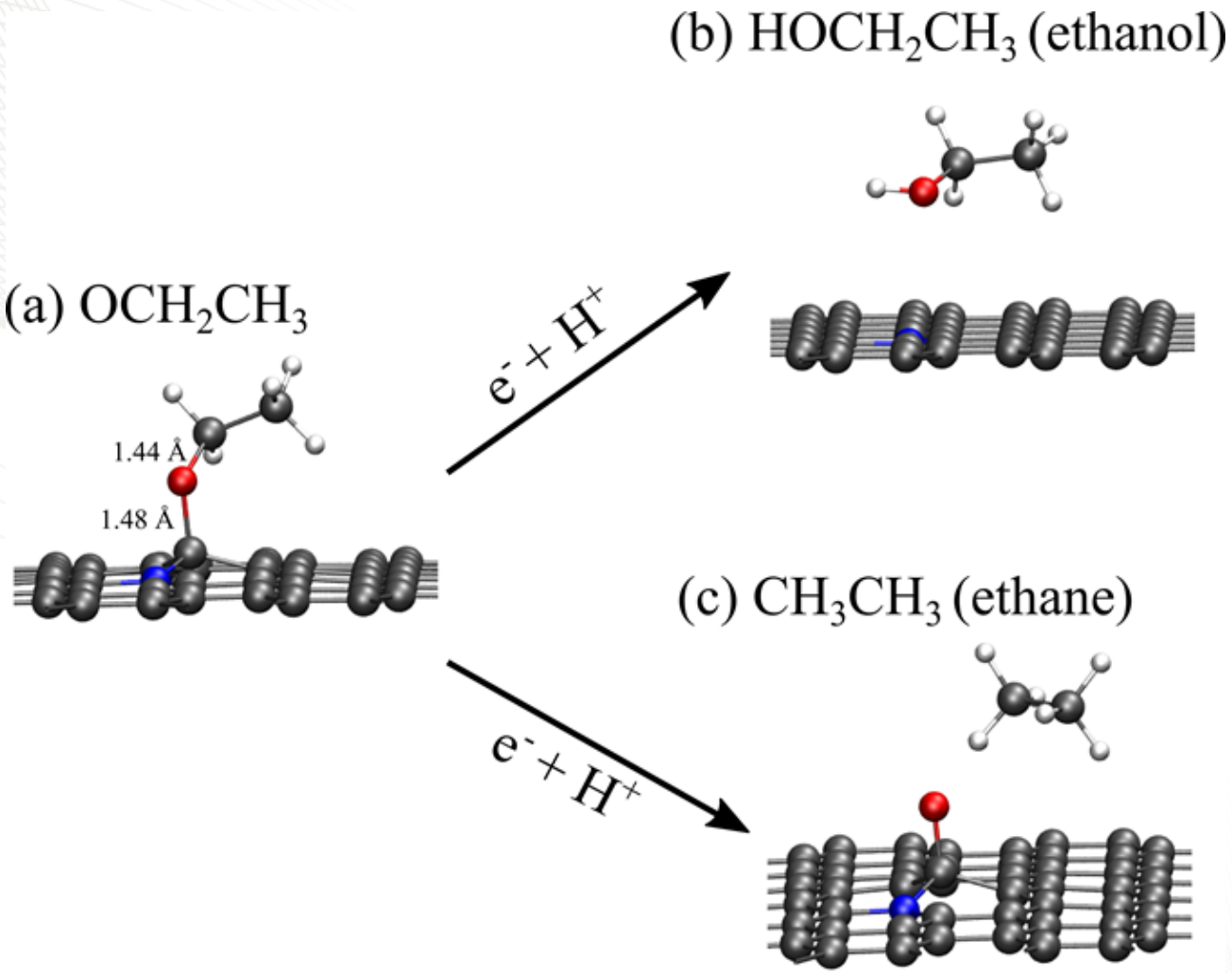
Binding energy: 0.74 eV



- N dopant: increased binding energy with OCCO.
- Local curvature increase binding energy between OCCO and graphene.

C2 intermediates strongly adsorbed by CNS

DFT of last reduction step favors Ethanol

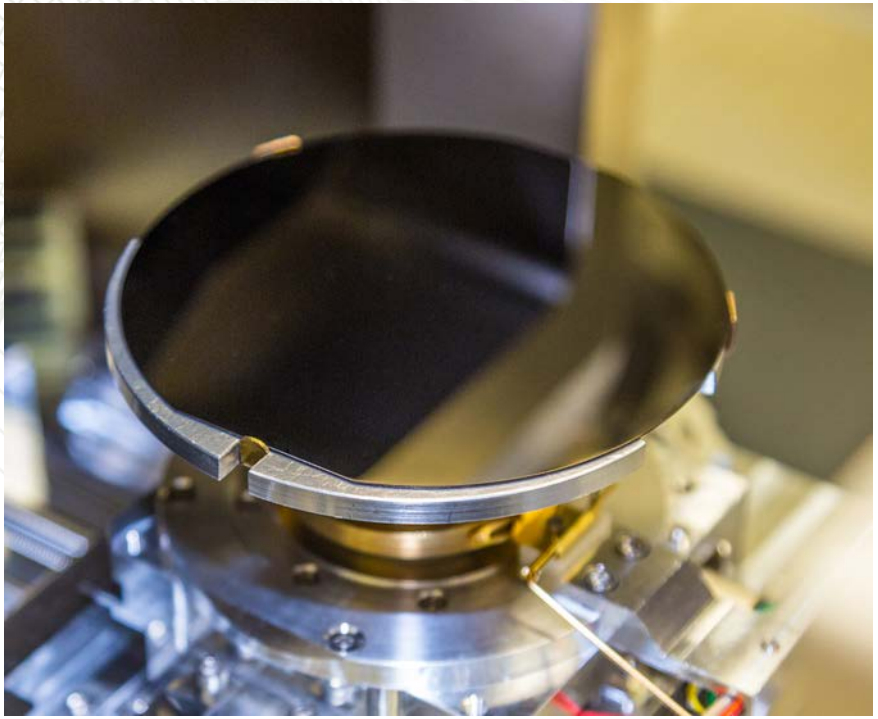


EtOH cleavage is much more energetically favorable (by 1.59 eV)

Technology Maturation Review

- Basic science performed under BES Scientific User Facility funding – that work continues
- Maturation funding from ORNL Technology Innovation (royalties)
  - Investigate scale up and lifetime but not novel application
  - Project has limited time and scope
- Fossil Energy project is complimentary and important
  - Investigating adaption of catalyst to alternative configurations

Maturation Work: Metallic Substrates

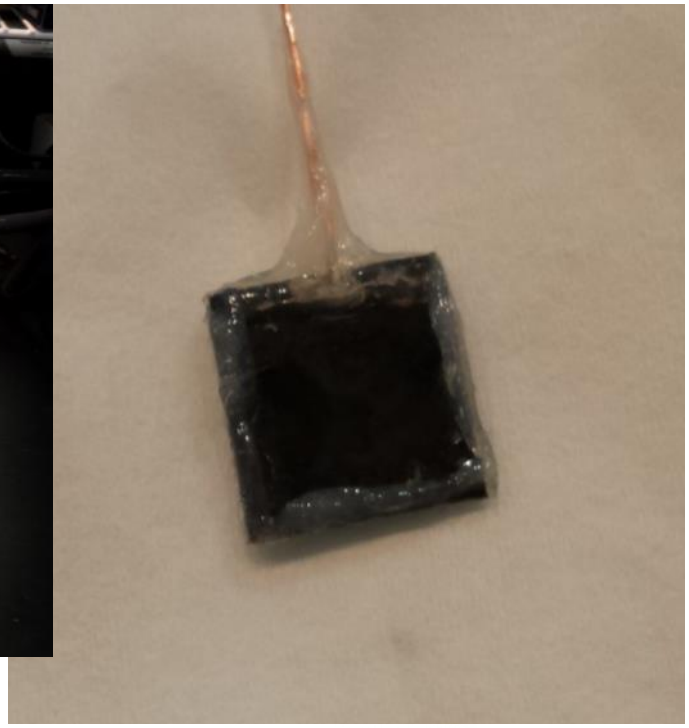


Original nanospikes grown on silicon wafers

Successfully growing nanospikes on metallic substrates

Large Format Electrochemistry Cells

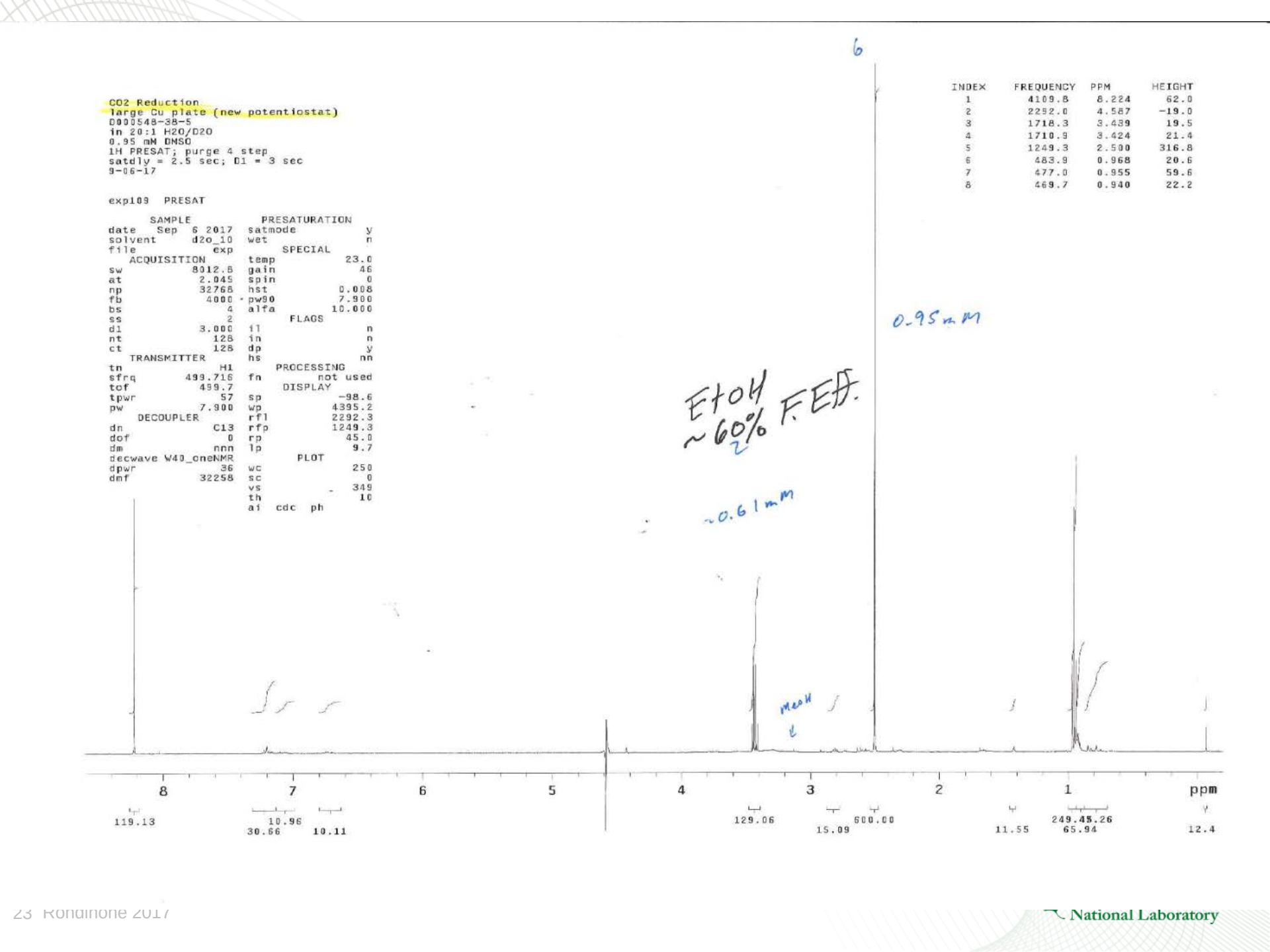
Demonstrator electrode = 100 cm^2



Research electrode = 1 cm^2

Large Format Results

- Ethanol Produced using a 100 cm^2 electrode
  - (0.6 mM conc. in 2 h of operation, ~60% F.E.)
- Ethanol Produced using an inexpensive substrate
  - Copper sheet at largest scale (100 cm^2)
  - 316 stainless on intermediate scale (2 cm^2 electrode)


6
CO2 Reduction
large Cu plate (new potentiostat)
D000548-38-5
in 20:1 H2O/D2O
0.95 mM DNSO
1H PRESAT; purge 4 step
satdly = 2.5 sec; D1 = 3 sec
9-06-17
exp109 PRESAT
SAMPLE
date Sep 6 2017
solvent d2o_10
file exp
ACQUISITION
sw 8012.8
at 2.045
np 32768
fb 4000
bs 4
ss 2
d1 3.000
nt 128
ct 128
TRANSMITTER
tn H1
sfrq 499.716
tof 499.7
tpwr 57
pw 7.900
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_oneNMR
dpwr 36
dmf 32258
PRESATURATION
satmode y
wet n
SPECIAL
temp 23.0
gain 46
spin 0
hst 0.008
pw90 7.900
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -98.6
wp 4395.2
rfl 2292.3
rfp 1249.3
rp 45.0
lp 9.7
PLOT
wc 250
sc 0
vs 349
th 10
ai cdc ph
INDEX FREQUENCY PPM HEIGHT
1 4109.8 8.224 62.0
2 2252.0 4.587 -19.0
3 1718.3 3.439 19.5
4 1710.9 3.424 21.4
5 1249.3 2.500 316.8
6 483.9 0.968 20.6
7 477.0 0.955 59.6
8 469.7 0.940 22.2
0.95 mM
EtOH
~60% F.E.
~0.61 mM
MeOH
8
7
6
5
4
3
2
1
ppm
119.13
10.96
30.66
10.11
129.06
15.09
600.00
11.55
249.45.26
65.94
12.4

Fossil Energy FWP: FEAA132

- Objectives
  - Raise the current density
    - Electrode structure, non-planar configurations
  - Evaluate and optimize operation within a fossil fuel combustion flue gas
    - Will demonstrate technical feasibility, if possible
    - Will investigate poisoning mechanisms, if they exist
    - Will investigate mitigation or pre-treatment strategies

Project Schedule and Budget

				FY2017	FY2018			
	Start Date	End Date	Cost	4	1	2	3	4
Task 1. Project Management and Planning*	8/15/2017	7/31/2018						
Quarterly report				12/31/17	3/31/28	6/31/18		
Comprehensive Final Report							7/31/18	
Task 2.1 Maximize current density of catalyst for production of ethanol – 3D electrode development	8/15/2017	9/30/2017	$71,000					
Task 2.2. Maximize current density of catalyst for the production of ethanol – 3D electrode, gas phase operation, maximize wettability	10/1/2017	7/31/2018	$49,000					
Milestone: Configure catalyst for gas phase operation					1/31/28		7/31/18	
Milestone: Complete maximization of current density of catalyst								
Task 3. Measure and optimize performance in flue gas	11/1/2018	7/31/2018	$80,000					
Milestone: Test and optimize catalyst against flue gas impurities					3/31/2018			
Milestone: Complete characterization of impurity intolerances							7/31/18	

	Fiscal Year 1				Fiscal Year 2					
	8/15/17 – 9/30/17		10/1/17 – 12/31/17		1/1/18 – 3/31/18		4/1/18 – 6/30/18		7/1/18 – 7/31/18	
	Q1	Total Project	Q2	Total Project	Q3	Total Project	Q4	Total Project	Q5	Total Project
Federal Share	$71,000	$71,000	$33,000	$104,000	$43,000	$147,000	$43,000	$190,000	$10,000	$200,000
Total Planned	$71,000	$71,000	$33,000	$104,000	$43,000	$147,000	$43,000	$190,000	$10,000	$200,000

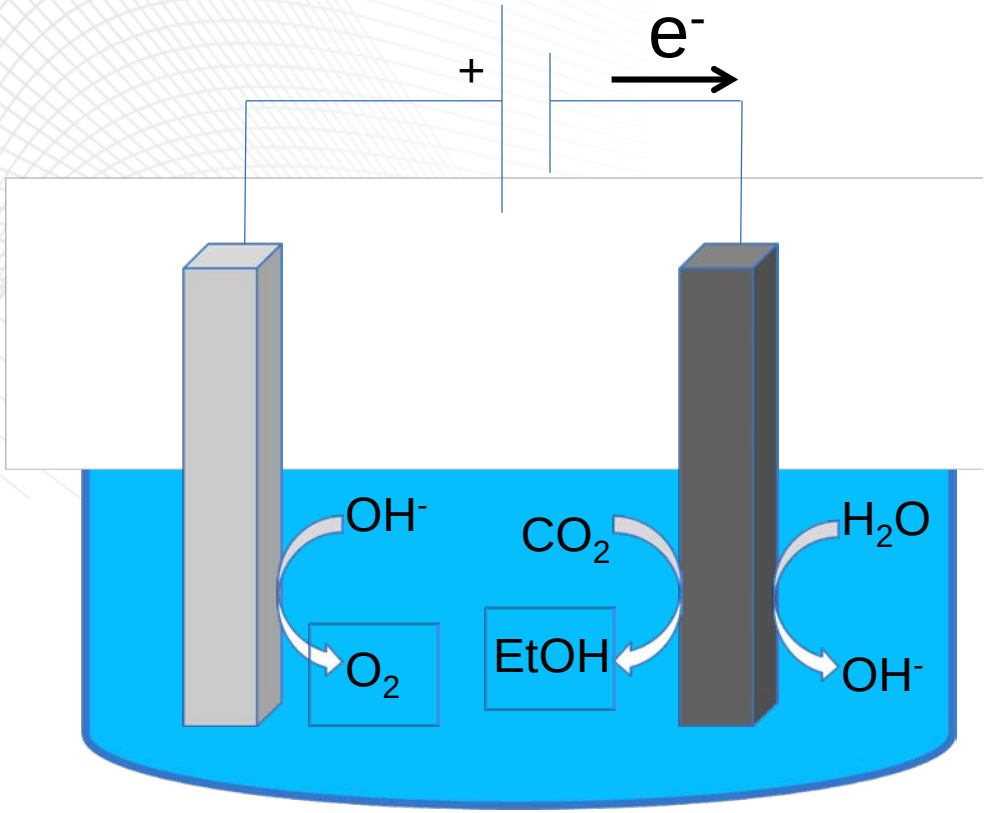
Obj. 1: Maximizing Current Density

- Current density = electrochemical activity of the catalyst
  - Battery analogue = amps
  - Measure using mA/cm^2, or electrical current per area of the catalyst
    - ARPA-e targets 300 mA/cm^2; we have achieved about ~15 mA/cm^2
  - Directly applicable to capital costs
    - Not competitive in fuel market right now
    - Fine chemicals/beverage market may be accessible soon
- Strategy
  - Adapt catalyst to better electrolytes, different cell and current-collector designs in order to maximize mass transport
    - CO_2 solubility
    - Wetting of the catalyst surface
    - Increased geometric surface are using 3D electrodes
    - Attempt implementation of gas-phase mass transport
    - Temperature and pressure

Other Strategies for Maximizing Current Density

- CNS on carbon cloth – amenable to gas phase and consistent with H_2 fuel cell construction
- Explore alternative electrolytes
  - Requirements are:
    - High CO_2 solubility as a molecule, not ion
    - Wide electrochemical stability window
    - Ability to solubilize salt for electric charge screening
    - Increased wettability (less polar than water)
  - Likely candidates include battery electrolytes
    - Dimethyl carbonate, glymes, acetonitrile

Current Density and Mass Transport

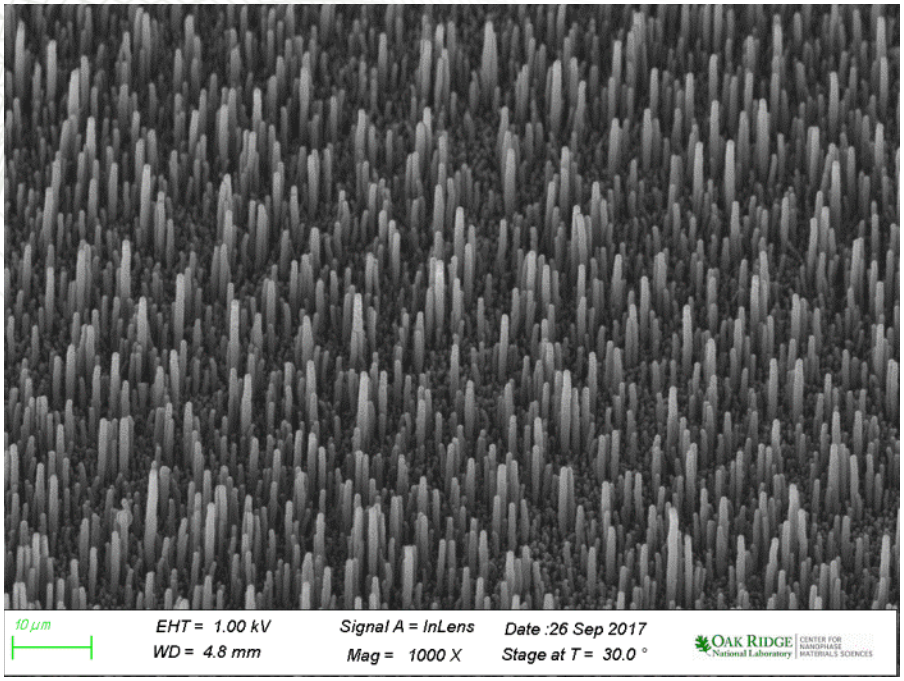


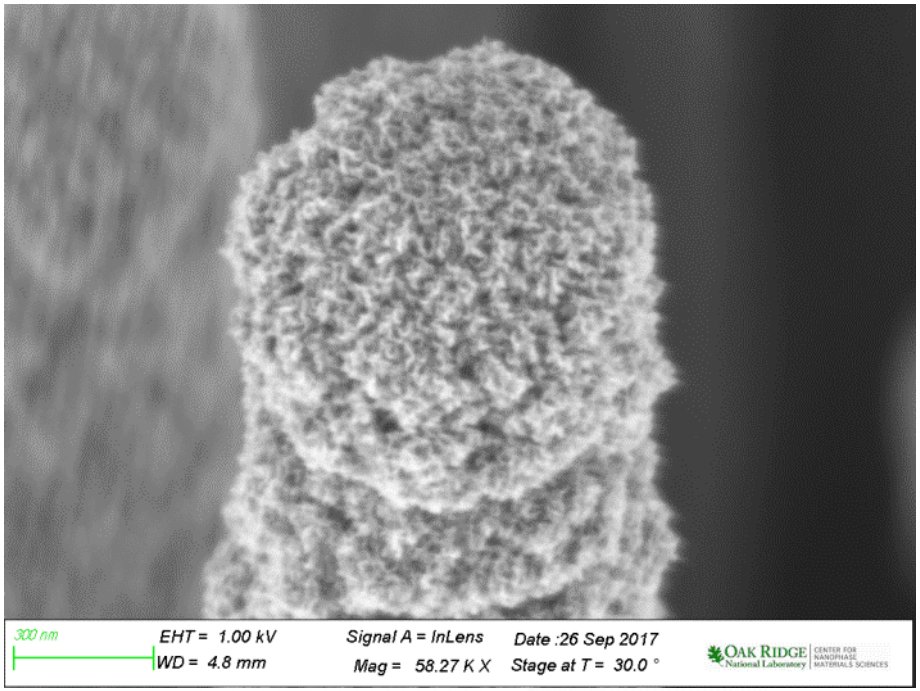
- Mass transport:
  - How quickly reagents can be brought to, and products carried away from, the catalyst surface
  - Is fundamental limitation in electrochemistry
  - Controlled by electrolyte and cell design
  - Influenced by temperature, pressure, concentration

- Today's catalysts commonly operate in $KHCO_3$
- Solubility high, but not as free CO_2
- Rate-limiting step is chemisorption of CO_2 from bicarbonate ion to catalyst surface

Alternative Substrates and Current Collectors

- Deposition of CNS on vertically aligned carbon fibers
- Requires a metallic substrate to seed tall fibers





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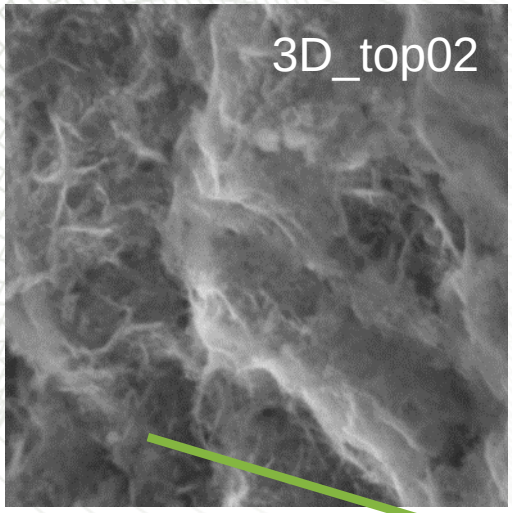
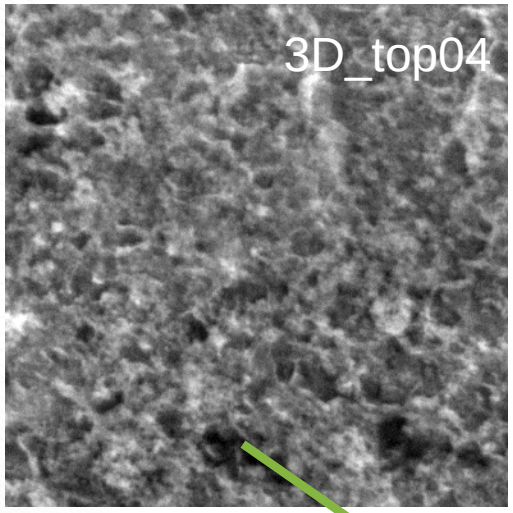
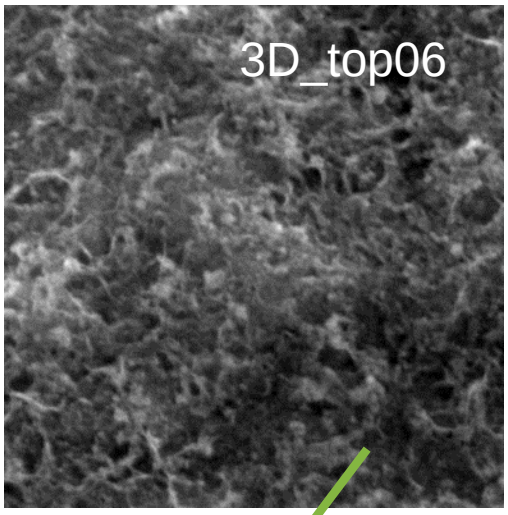
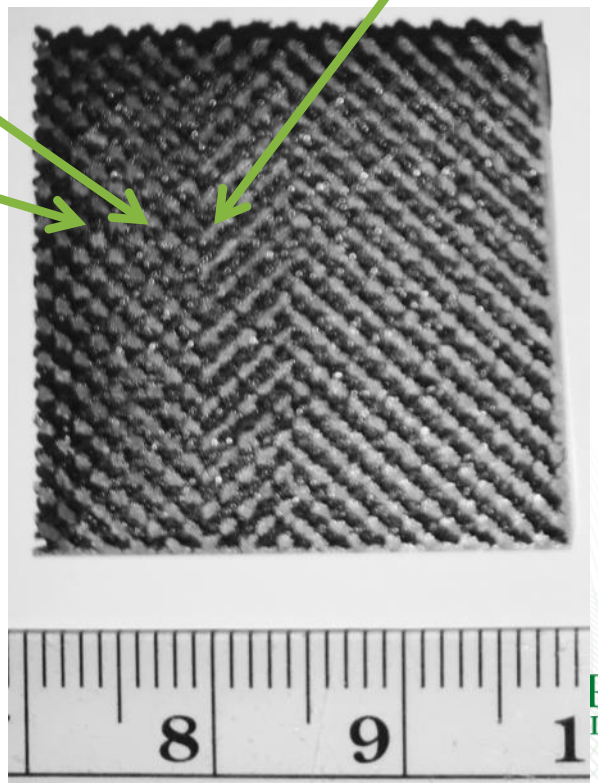
Growth of CNS on a 3D printed mesh





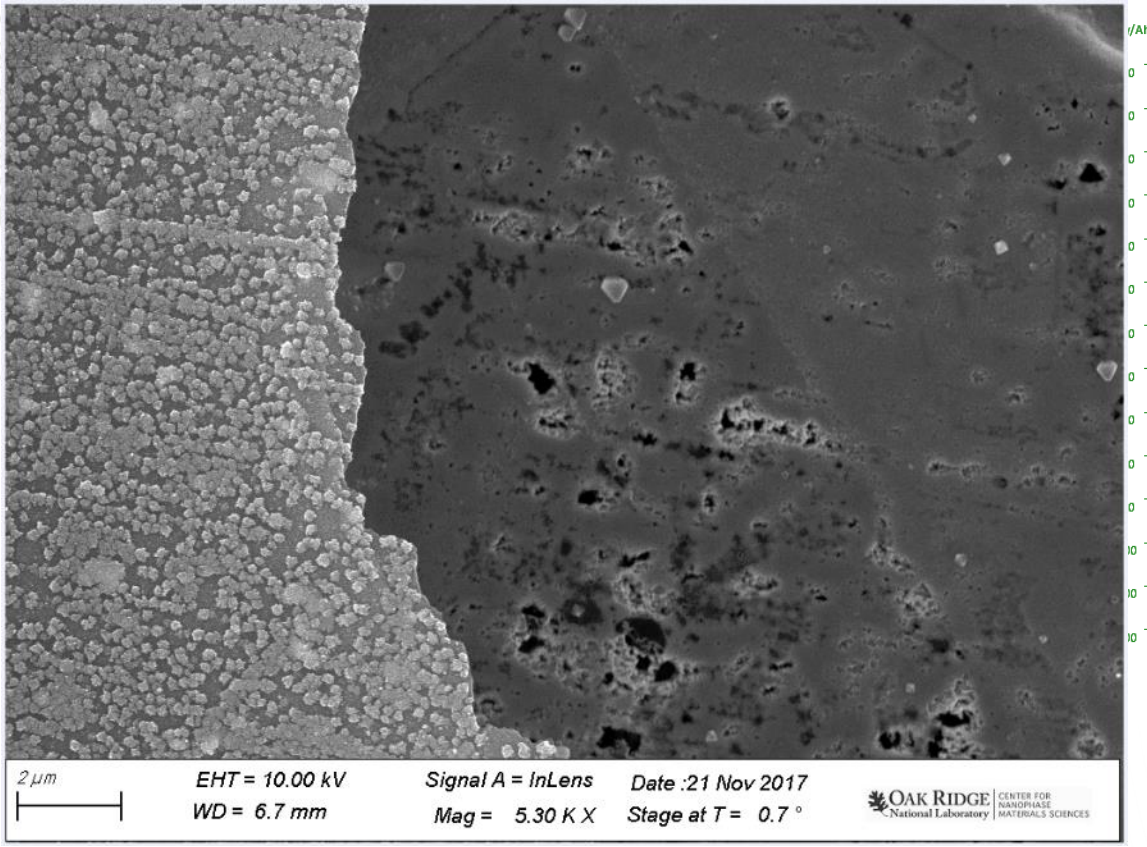


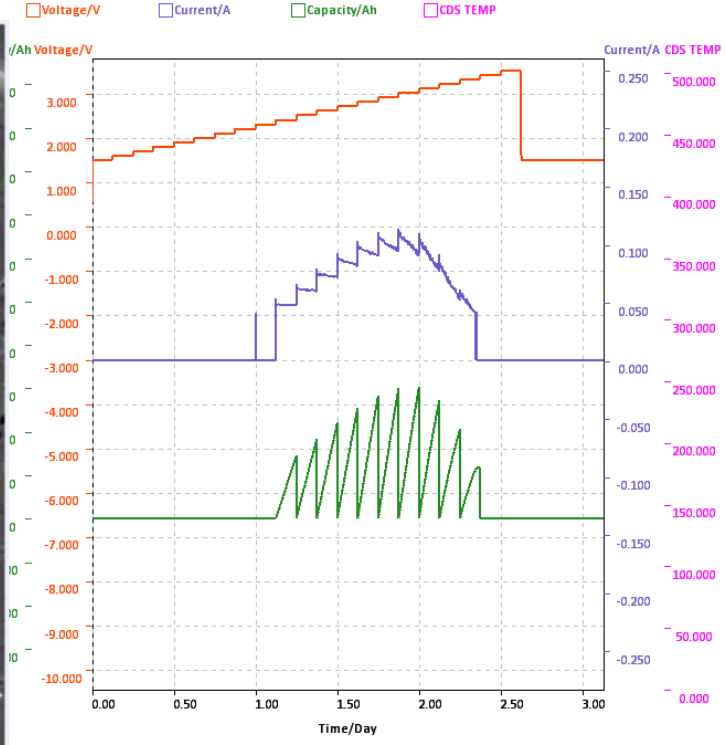
- Enhanced surface area
- Potential route to gas phase operation
- CNS were observed ~ 3 mm from the edge;
- A carbon film without clear CNS feature was observed further inside till ~8 mm from the edge.



Metallic Substrates are Unstable Long Term

- Carbon nanospike (catalyst) layer is generally stable
- Metallic substrates subject to remodeling which causes delamination





Only became obvious with extended runs

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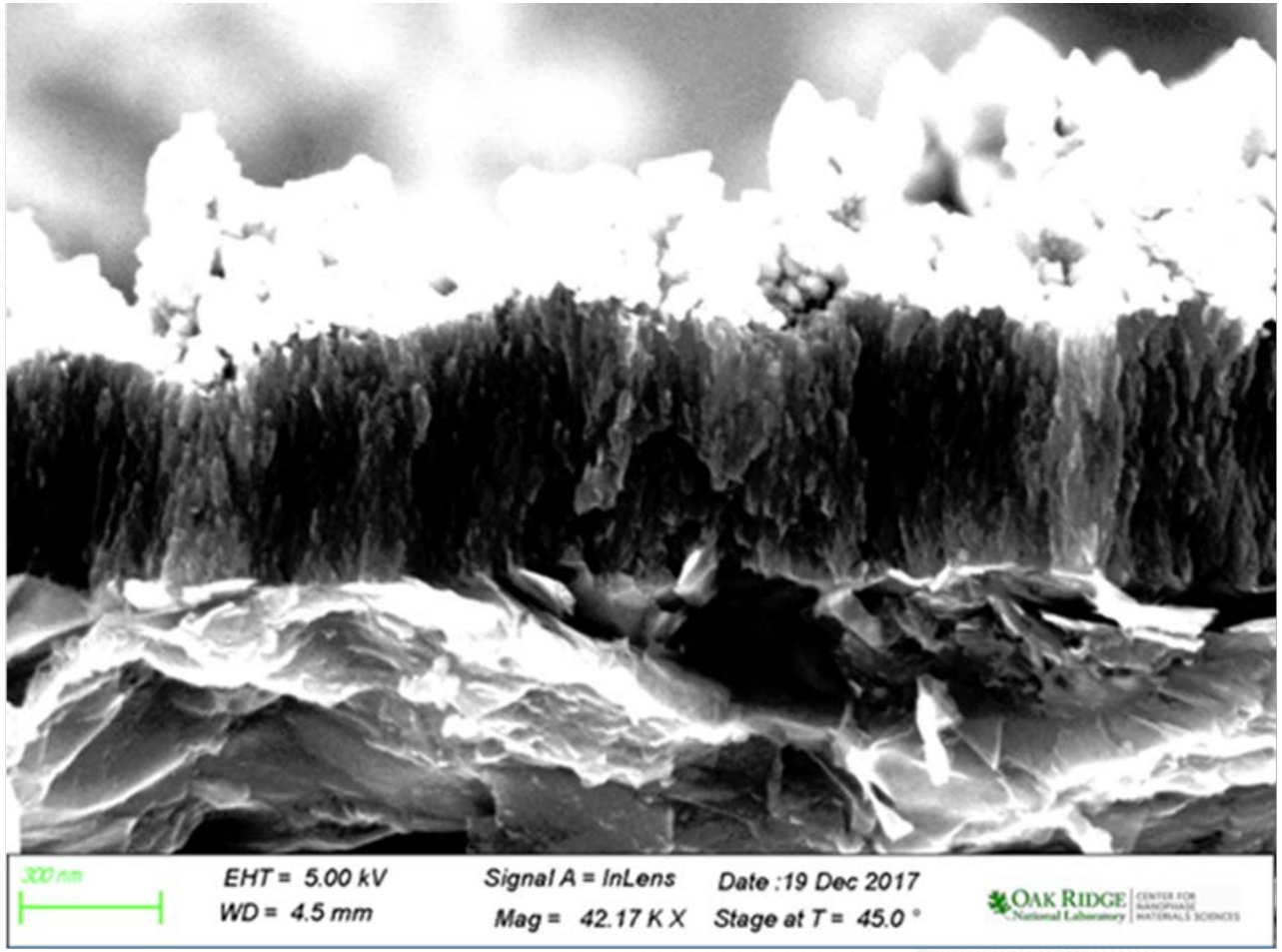
Graphite is Not Subject to Remodeling

Graphite and carbon fiber are stable after extended runs

Cost is very reasonable

No possibility for substrate ion migration



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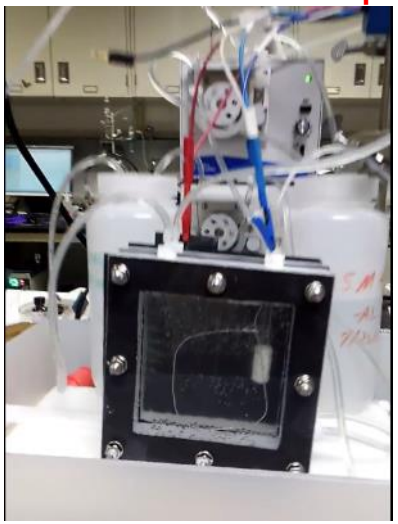
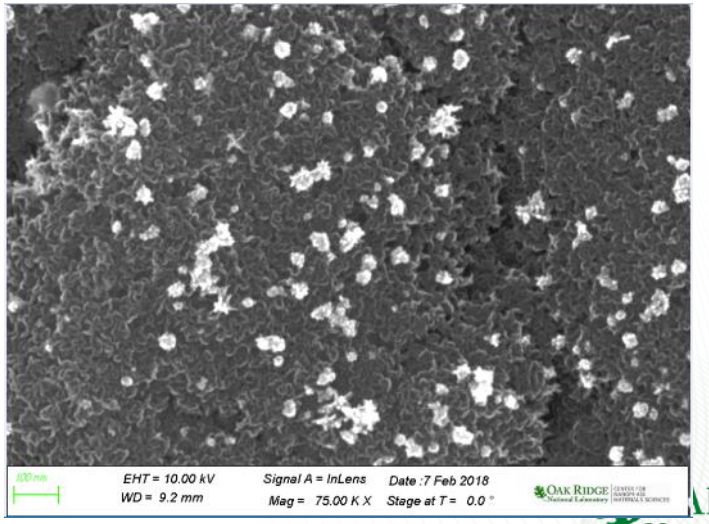
Durability testing

- The base carbon nanospike layer (without the copper co-catalyst) has been tested at high potential (-5V) to 300 hours on graphite.
  - Accelerated aging study was conducted at 5V for 300 h with no degradation of the CNS layer.
    - Nanospikes and carbon layer showed no sign of degradation – still sharp
    - Generally we will run the catalyst at a lower potential for the best Faradaic efficiency

100cm^2 cell in operation



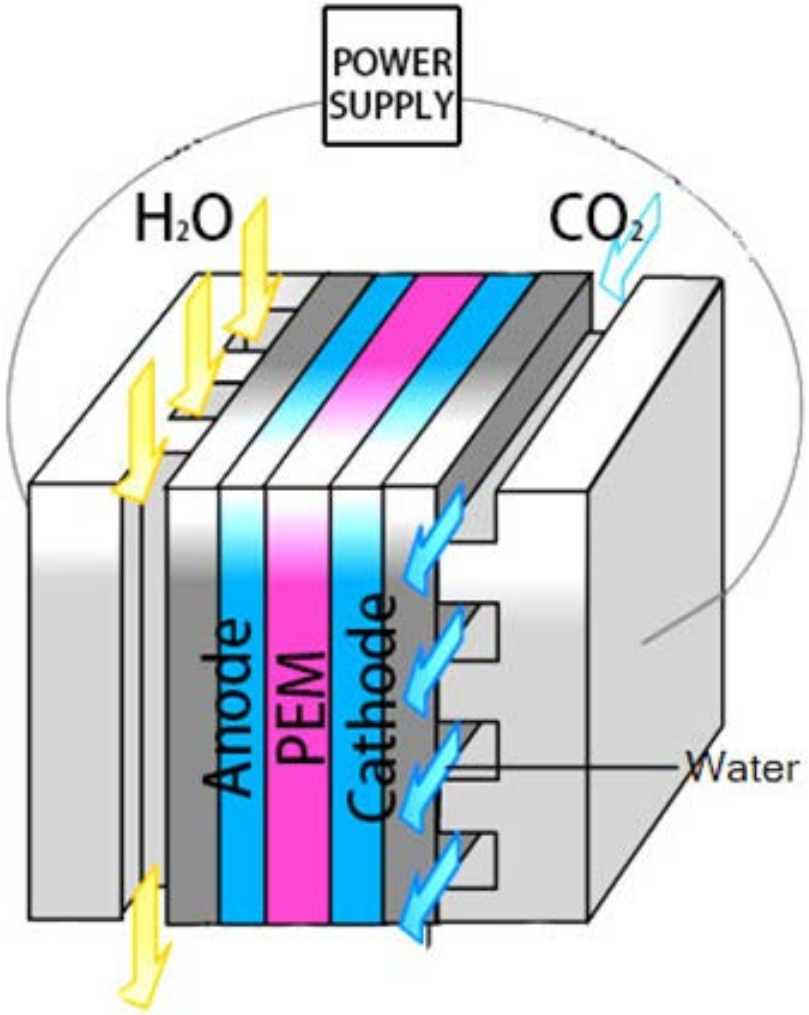
CNS after 300 hours of accelerated aging (5 Volts)



Vapor Phase Operation

Vapor or gas phase operation is a significant pathway towards increased current density

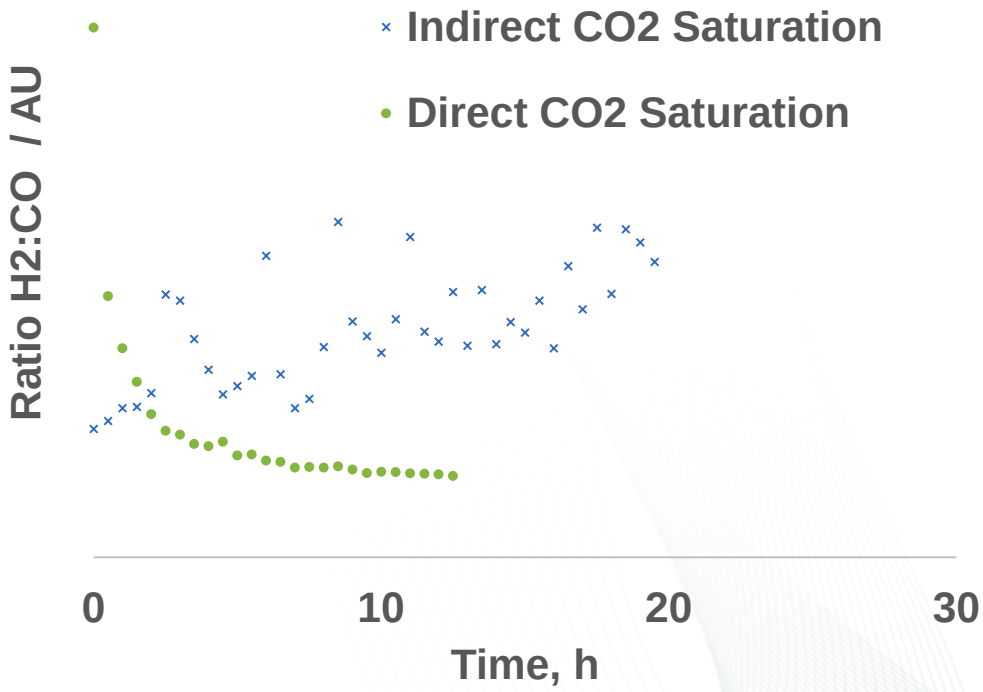
At start of this project we were not sure that our mechanism was compatible



Will Vapor Phase CO_2 React?

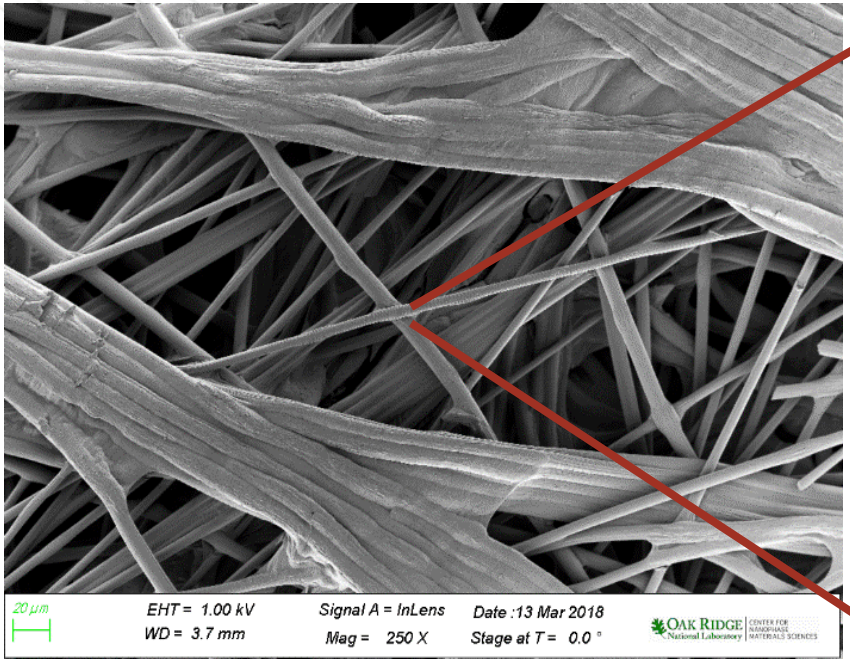
- We have determined that the reaction likely proceeds via dissolved CO_2 and not bicarbonate, in contrast to we originally proposed.
- This has positive implications for running in the vapor phase
- Potentially higher activity at elevated pressure

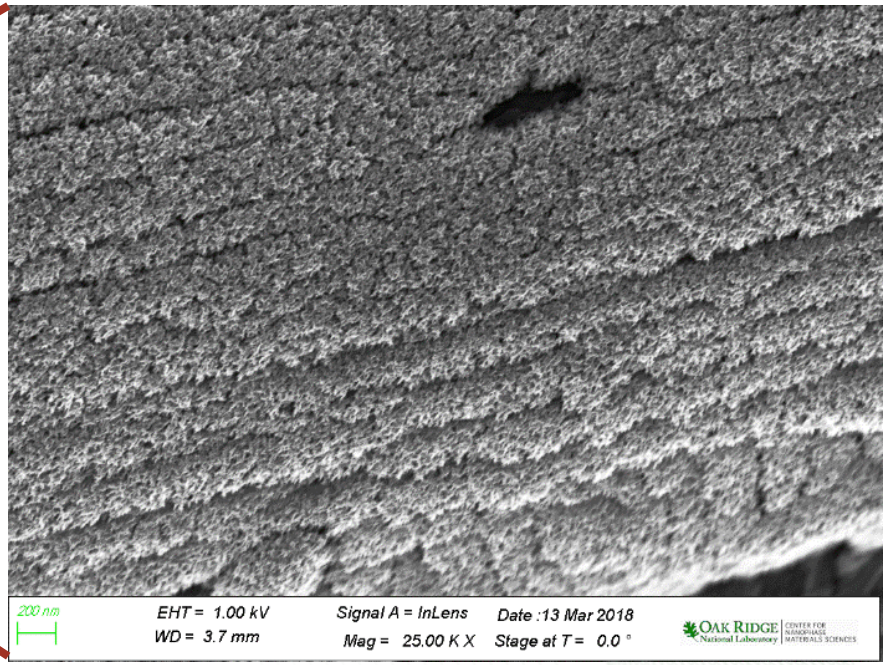
Chronoamperometry (5 Volts) study of plain carbon nanospikes on graphite with direct and indirect CO_2 saturation. Carbon nanospikes without copper co-catalyst make syngas.



Gaseous Diffusion Layer

- Stability on graphite means that carbon cloth can also be used
- Forms a gas diffusion electrode (GDE)
- Coating depth is limited due to plasma deposition process
- Appears to coat several microns into the carbon cloth, which should be sufficient





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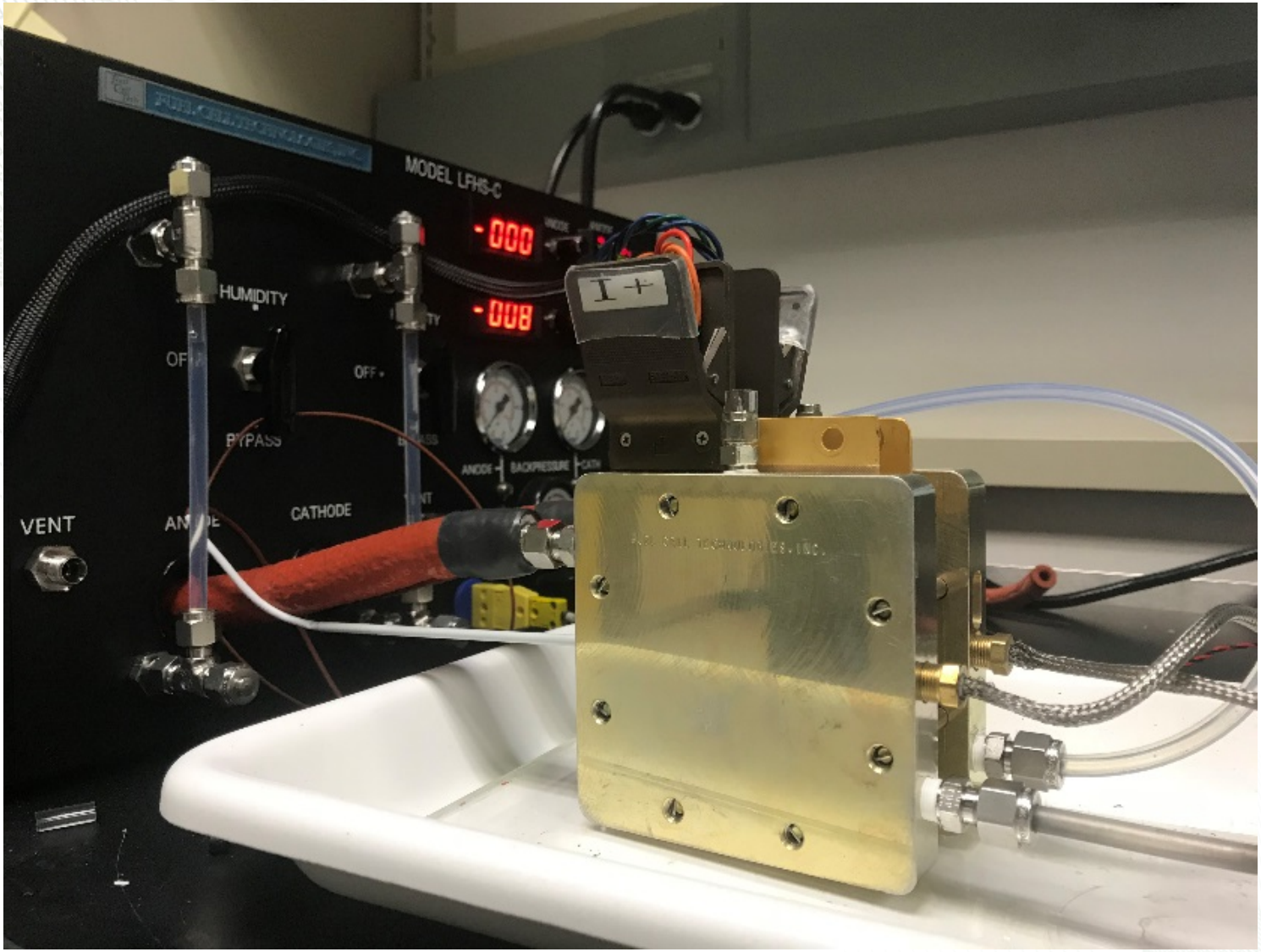
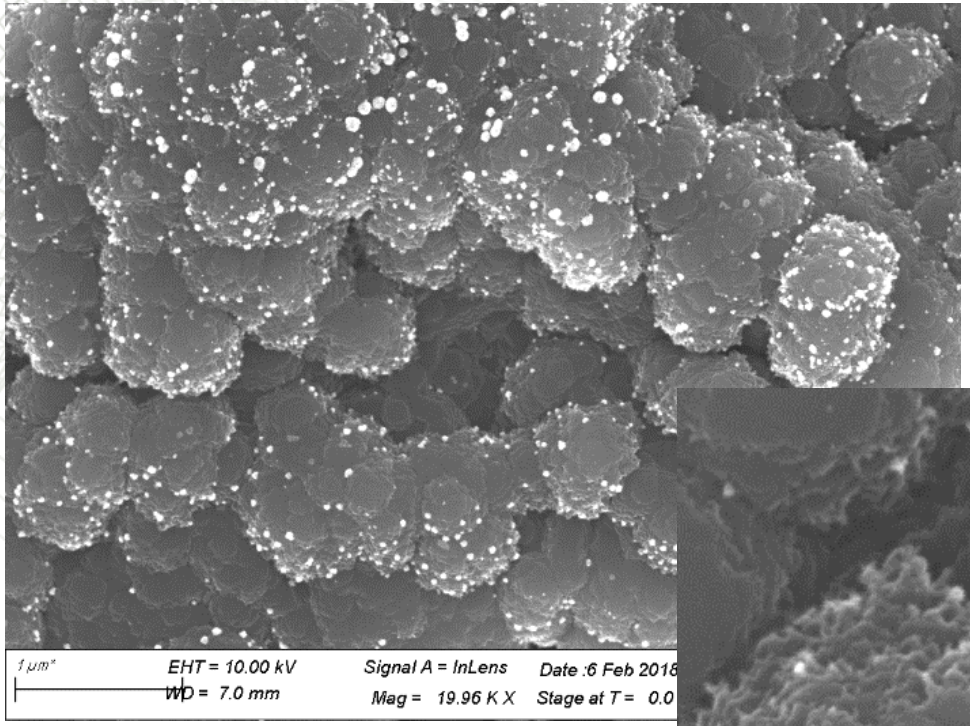
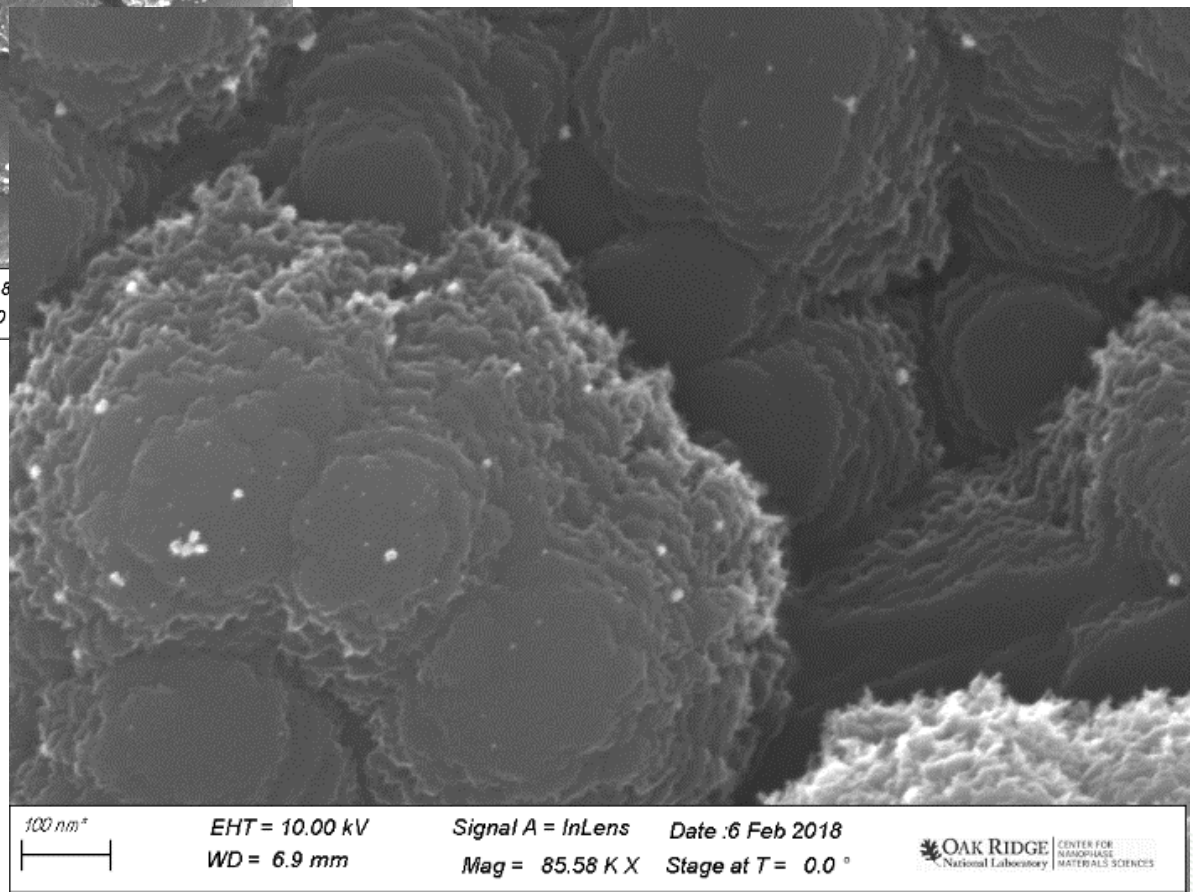
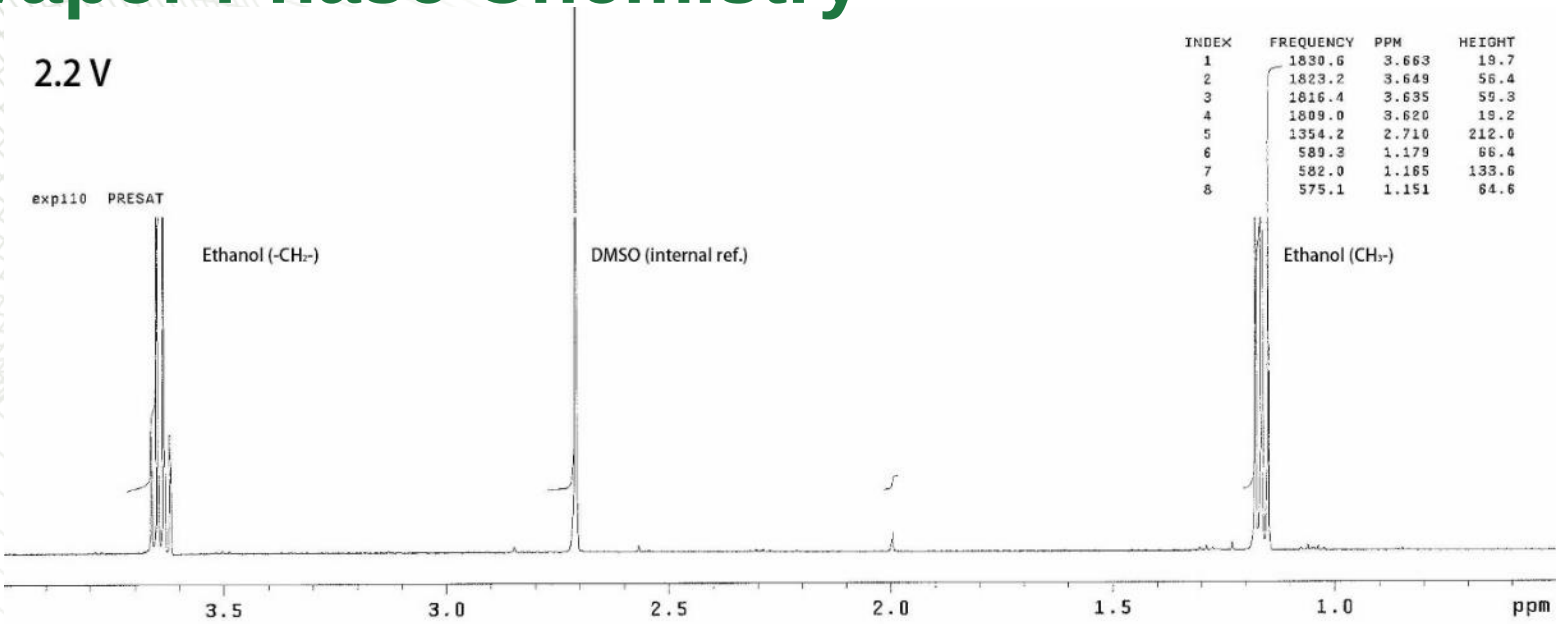


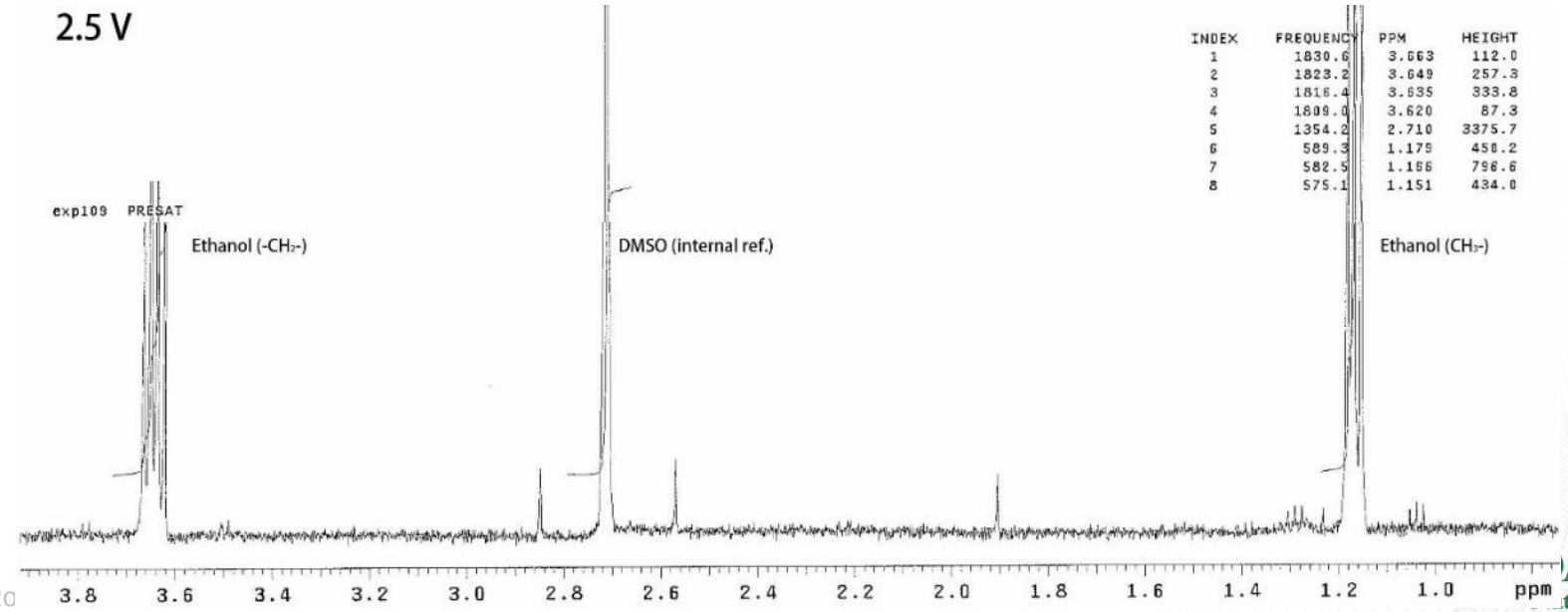
Gas Diffusion Durability

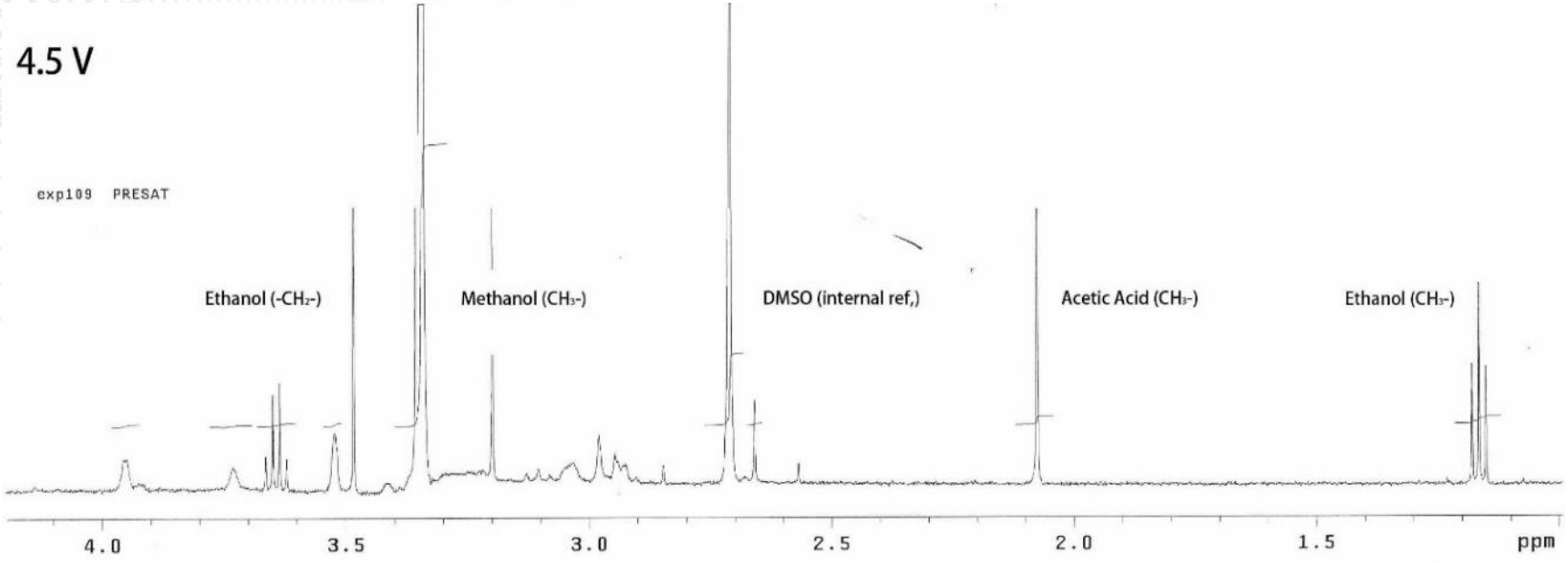




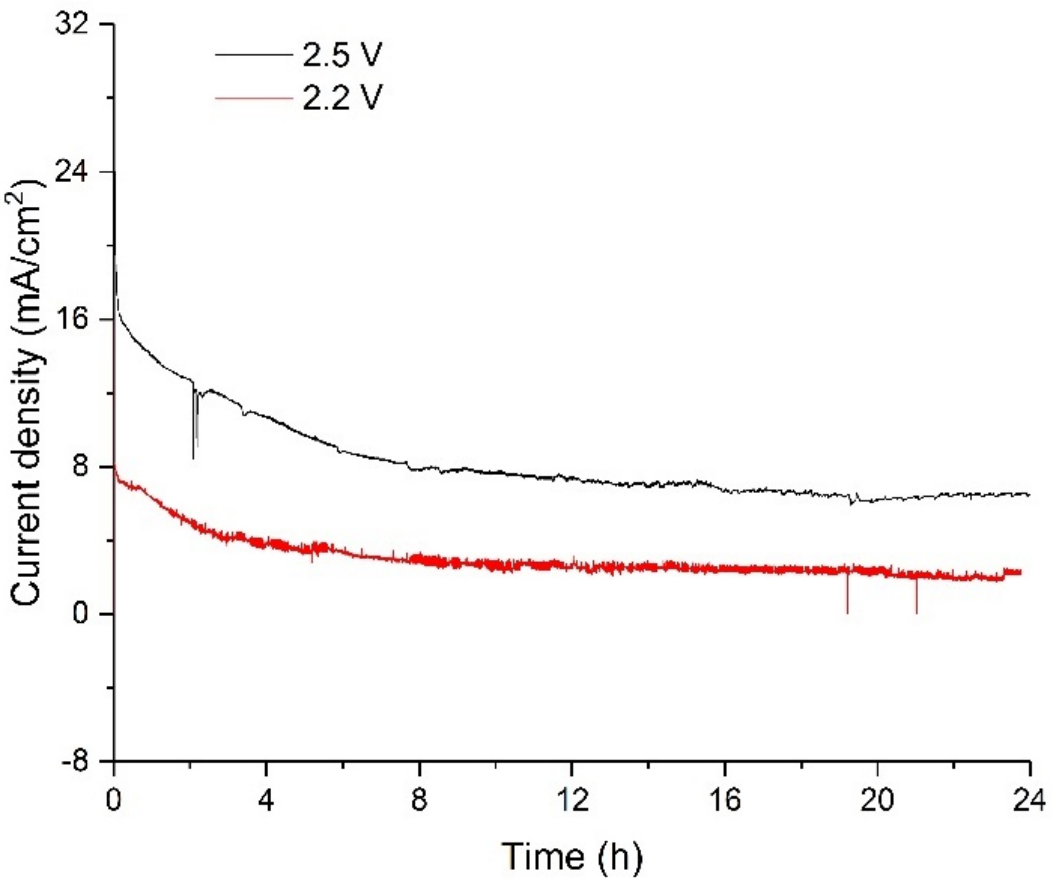
Vapor Phase Chemistry

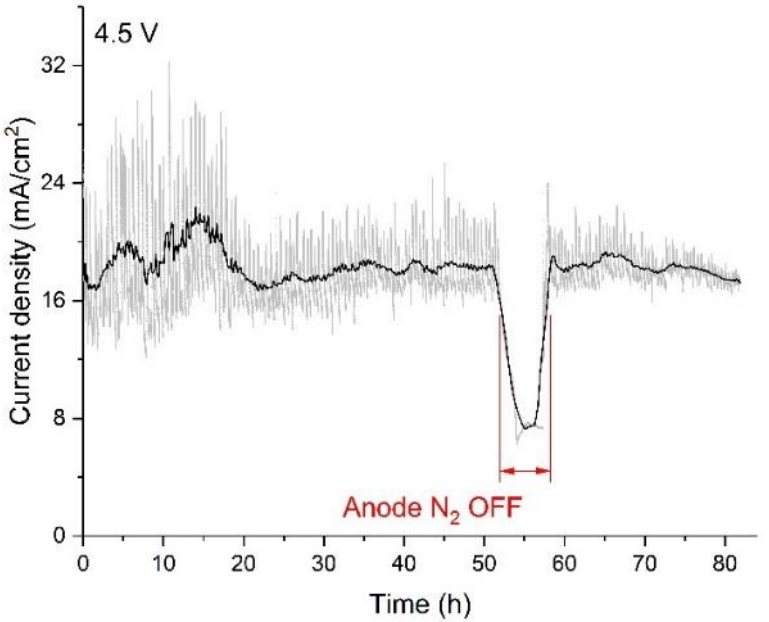






Vapor Phase Stability with Time





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What this means for Current Density

- Current density is higher than in water electrolyte, but still too low for practical application
- There are a large number of variables that must be optimized and we have not yet had the time to do so.
  - Temperature of cell (1)
  - Humidity and flow rate for each compartment (4)
  - Backpressure for each compartment (2)
    - 7 variables just for physical conditions
- Hydration control is a major issue that is largely unresolved
  - Sargent recently published vapor phase cell with KOH electrolyte between Teflon-soaked GDE and membrane

Summary of Current Density Studies

- Vapor phase operation is possible and a likely avenue to success
  - Other researchers (Opus 12, Ted Sargent) have demonstrated high current density in vapor phase
  - CO dimerization is possible in vapor phase
  - Current density is still low due to large unoptimized phase space
  - Hydration control remains a major issue
- Going forward:
  - Mechanism appears to work as expected!
  - Continue to study hydration control
    - Also need to study counterion contribution
  - Membranes are not proven.
    - Nafion is the primary membrane for vapor phase but inappropriate for CO_2 chemistry

Obj. 2: Test and Optimize Within Flue Gas

- Real world flue gas contains myriad contaminants
- Cost depends on pre-treatment needs
- Must understand impact of contaminants
- Some contaminants (CO, H_2O) may be beneficial to an electrochemical reaction

Table 2
Typical non-nitrogen components of untreated flue gases from Eastern Low Sulfur Coal

Species	Concentration
H_2O	5–7%
O_2	3–4%
CO_2	15–16%
Hg complexes	1 ppb
CO	20 ppm
Various hydrocarbons	10 ppm
HCl	100 ppm
SO_2	800 ppm
SO_3	10 ppm
NO_x	500 ppm

Data from Ref. [37].

C.E. Powell, G.G. Qiao / Journal of Membrane Science 279 (2006) 1–49

Some Contaminants We Already Understood

- O_2 is a possible etchant of the nanospikes
- N_2 we know is reactive with the nanospikes and forms NH_3

SCIENCE ADVANCES | RESEARCH ARTICLE

ELECTROCHEMISTRY

A physical catalyst for the electrolysis of nitrogen to ammonia

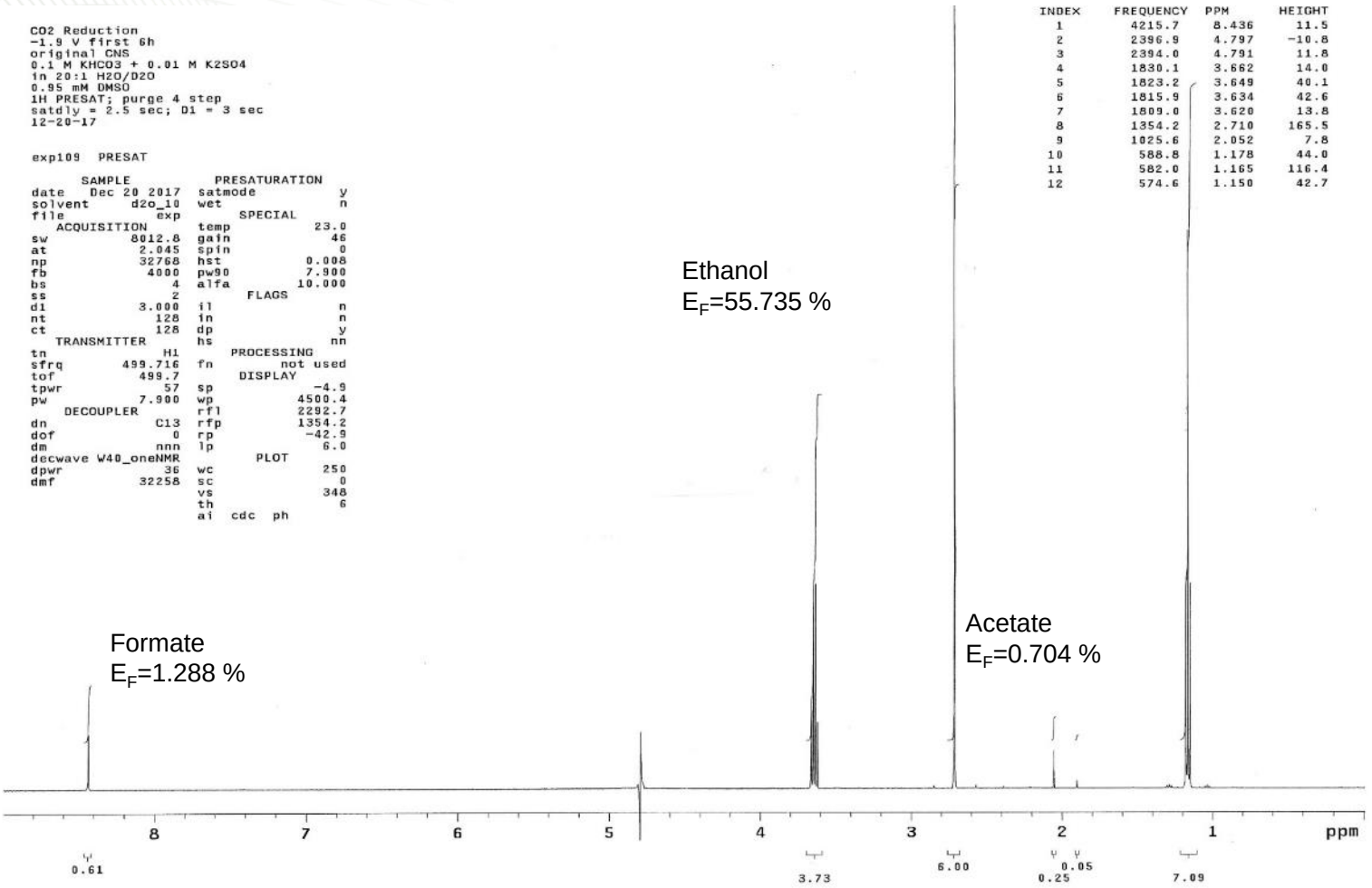
Yang Song,[1] Daniel Johnson,[1] Rui Peng,[1] Dale K. Hensley,[1] Peter V. Bonnesen,[1] Liangbo Liang,[1] Jingsong Huang,[1,2] Fengchang Yang,[3] Fei Zhang,[3] Rui Qiao,[3] Arthur P. Baddorf,[1] Timothy J. Tschaplinski,[4] Nancy L. Engle,[4] Marta C. Hatzell,[5] Zili Wu,[1,6] David A. Cullen,[7] Harry M. Meyer III,[7] Bobby G. Sumpter,[1,2] Adam J. Rondinone[1]*

Ammonia synthesis consumes 3 to 5% of the world's natural gas, making it a significant contributor to greenhouse gas emissions. Strategies for synthesizing ammonia that are not dependent on the energy-intensive and methane-based Haber-Bosch process are critically important for reducing global energy consumption and minimizing climate change. Motivated by a need to investigate novel nitrogen fixation mechanisms, we herein describe a highly textured physical

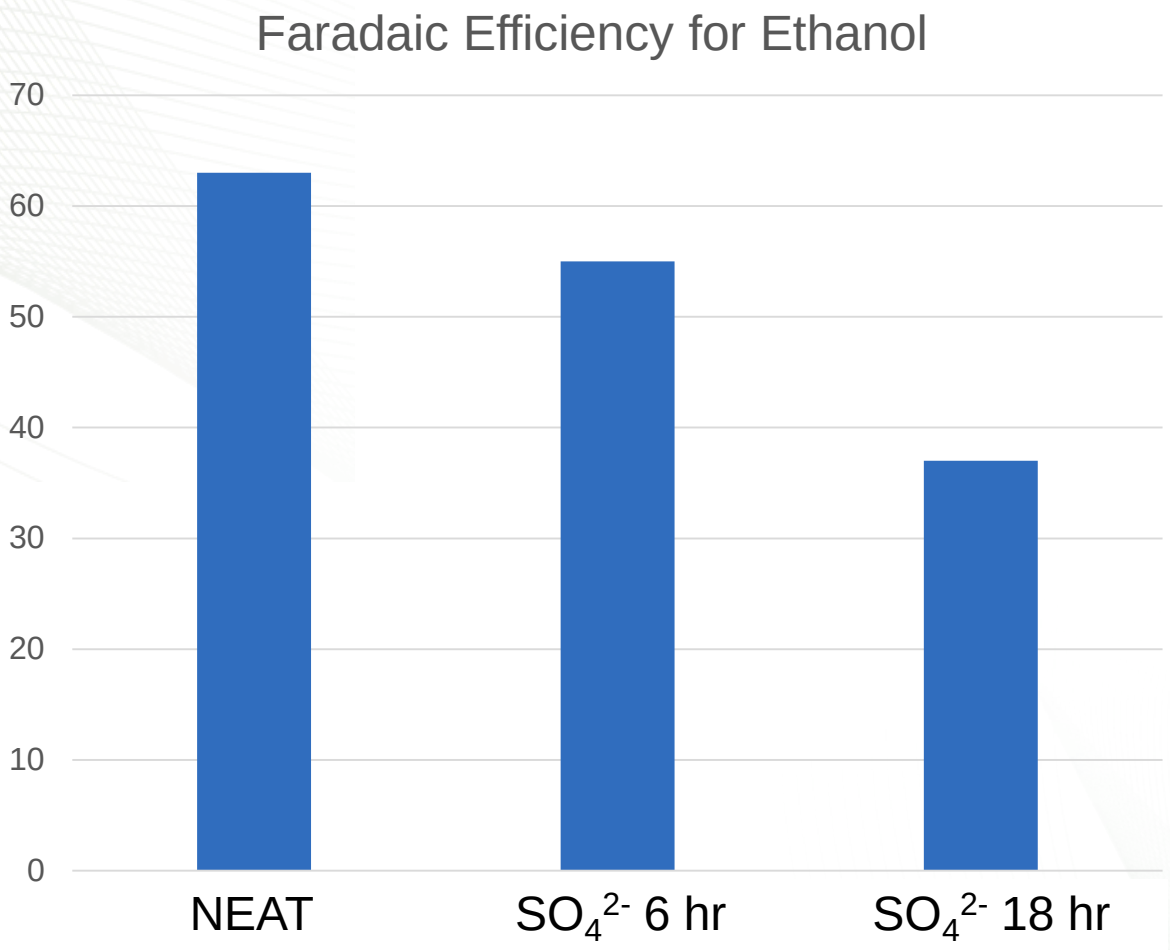
- This project: focus on SO_x and NO_x

Sulfur Contamination Tolerance

- Sulfate ion, as a proxy for SOx, slowly interferes with the reaction at 10 mM

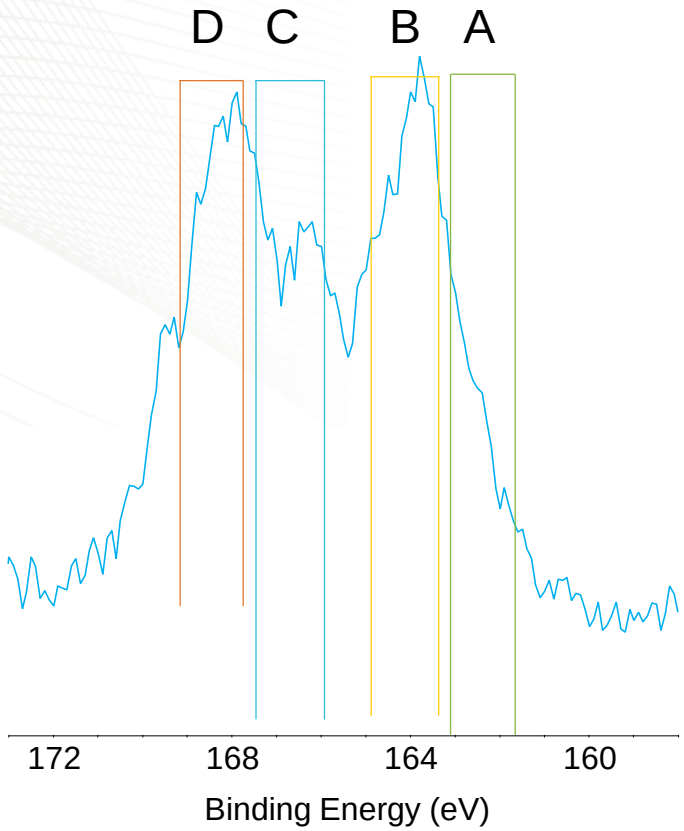


Effect of Sulfur



XPS Analysis of S-Contaminated Electrode

Cu-CNS



(A) B.E. = 162.0 eV
- metal sulfide, likely Cu-sulfide
- could be elemental S

(B) B.E. = 163.4 to 163.6 eV
- metal sulfide, likely Cu-sulfide

(C) B.E. = 165.8 eV to 166.4 eV
- SO_3^- or SO_2^-

(D) B.E. = 168.0 eV
- sulfate, SO_4^-

Sulfate Mechanism

$$SO_4^{2-} + 4H_2O + 8e^- \rightarrow 8OH^- + S^{2-}$$

$$Cu + S^{2-} \rightarrow CuS + 2e^-$$

- Copper sulfide or mixtures of sulfate/sulfide are found on the nanospike surface
- Reaction is inhibited
- Uptake of sulfur is slow and could be mitigated by periodic refreshing of the nanoparticles

NO_x Contamination Tolerance

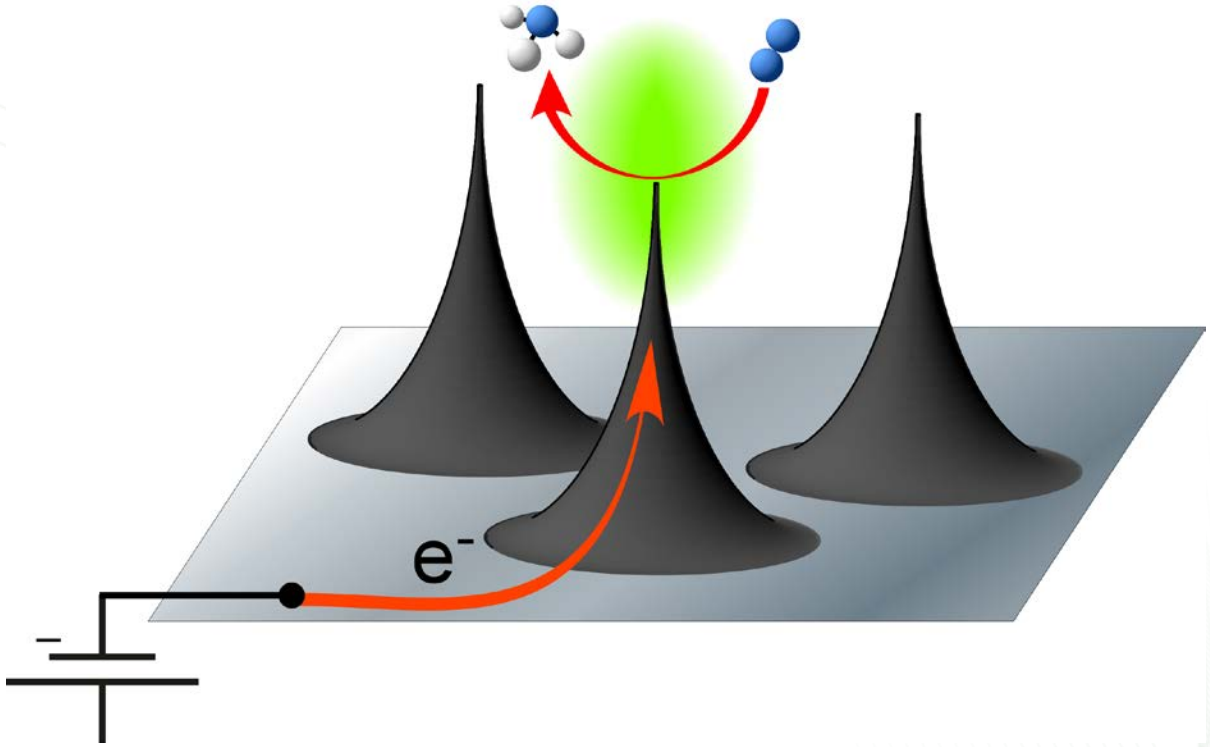
- Nitrogen in all forms appears to poison the reaction
- NO gas is a complete inhibitor
- NO_3^- is a complete inhibitor
- N_2 also fouls the reaction
  - Exposure of the cell to air during the reaction does not appear to be a problem due to low N_2 solubility
  - Introducing N_2 to the electrolyte with CO_2 fouls the reaction – it proceeds but not to ethanol

3 Years Ago – Discovered N_2 Reactivity

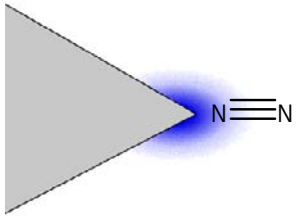
Can we use electricity instead of T and P?

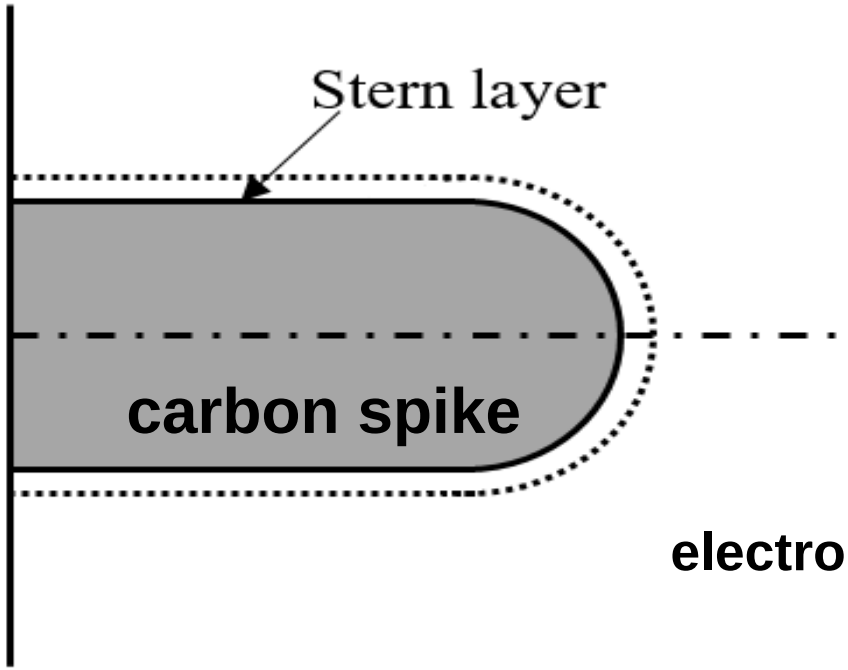
$$3H_2O + 2N_2 \xrightarrow{e^-} 3/2O_2 + 2NH_3$$

A high electric field can destabilize N_2



Modeling the field





Poisson-Nernst-Planck Equations

$$\nabla \cdot (-\epsilon_0 \epsilon_r \nabla \phi) = \rho_v$$
$$\rho_v = F(c_+ - c_-)$$
$$\nabla \cdot (-D\nabla c_i - u_i z_i F c_i \nabla \phi) = 0$$

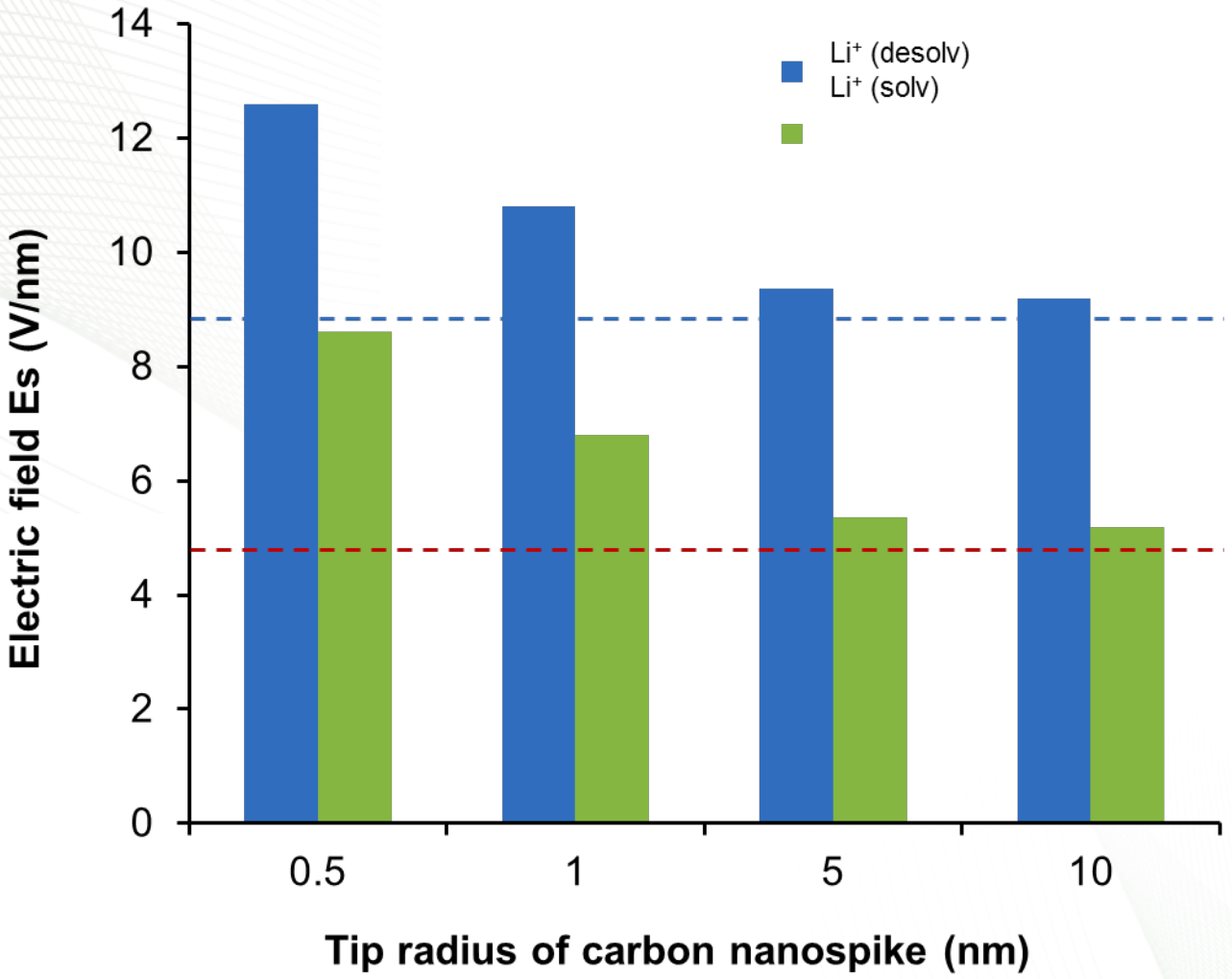
Parameters

$C_\infty = 0.1M$
$V_{tip} = 1V$
$\varepsilon_{Stern} = 8$
$\varepsilon_{bulk} = 78$

Solved using COMSOL Package

This slide funded by BES

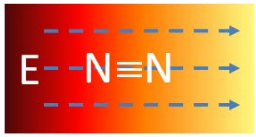
Amplification of Electrical Field at CNS Tip



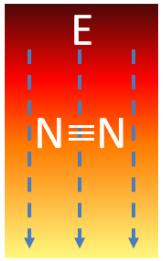
This slide funded by BES

Electron Propagator Theory (EPT) Calculations

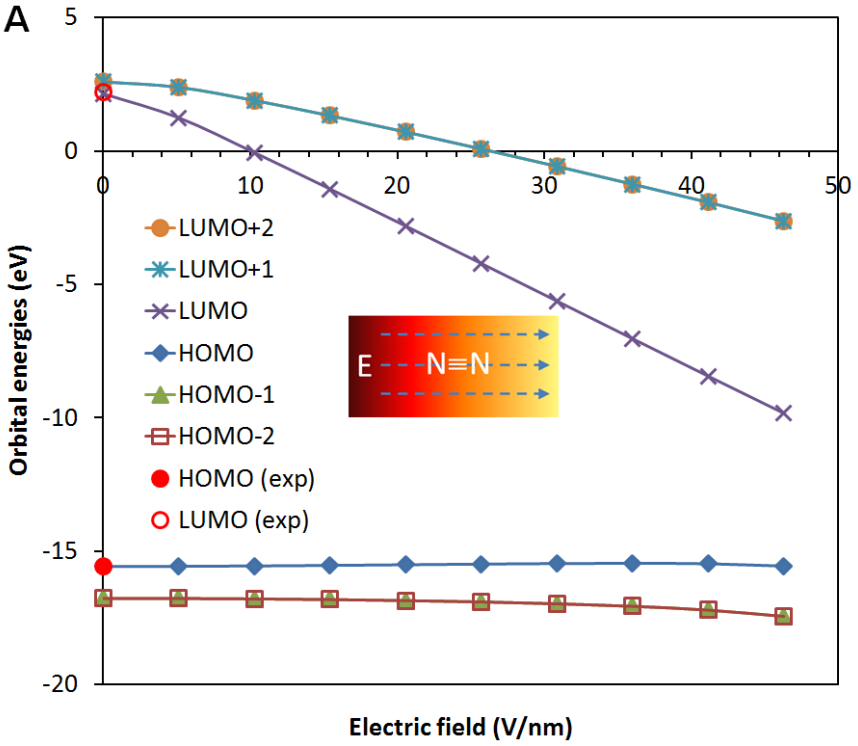
- Gaussian 09 program
- B3LYP/6-31G* for N_2 molecule optimization
- EPT/aug-cc-pVTZ (Outer Valence Green's Function)
- Longitudinal and transversal electric field
- Field strength 0.00-0.09 a.u. (0-4.628 V/Å)
- Ionization potentials (IPs) = -E(occupied)
- Electron affinities (EAs) = -E(unoccupied)



Longitudinal field ($E_{//}$)



Transversal field ($E_{\perp}$)



This slide funded by BES

Expect that Most Forms of N go to NH_3

$NO \rightarrow NH_3$

$NO_2 \rightarrow NH_3$

N_2O ?

$N_2 \rightarrow NH_3$

$NO_3^{2-} \rightarrow NH_3$

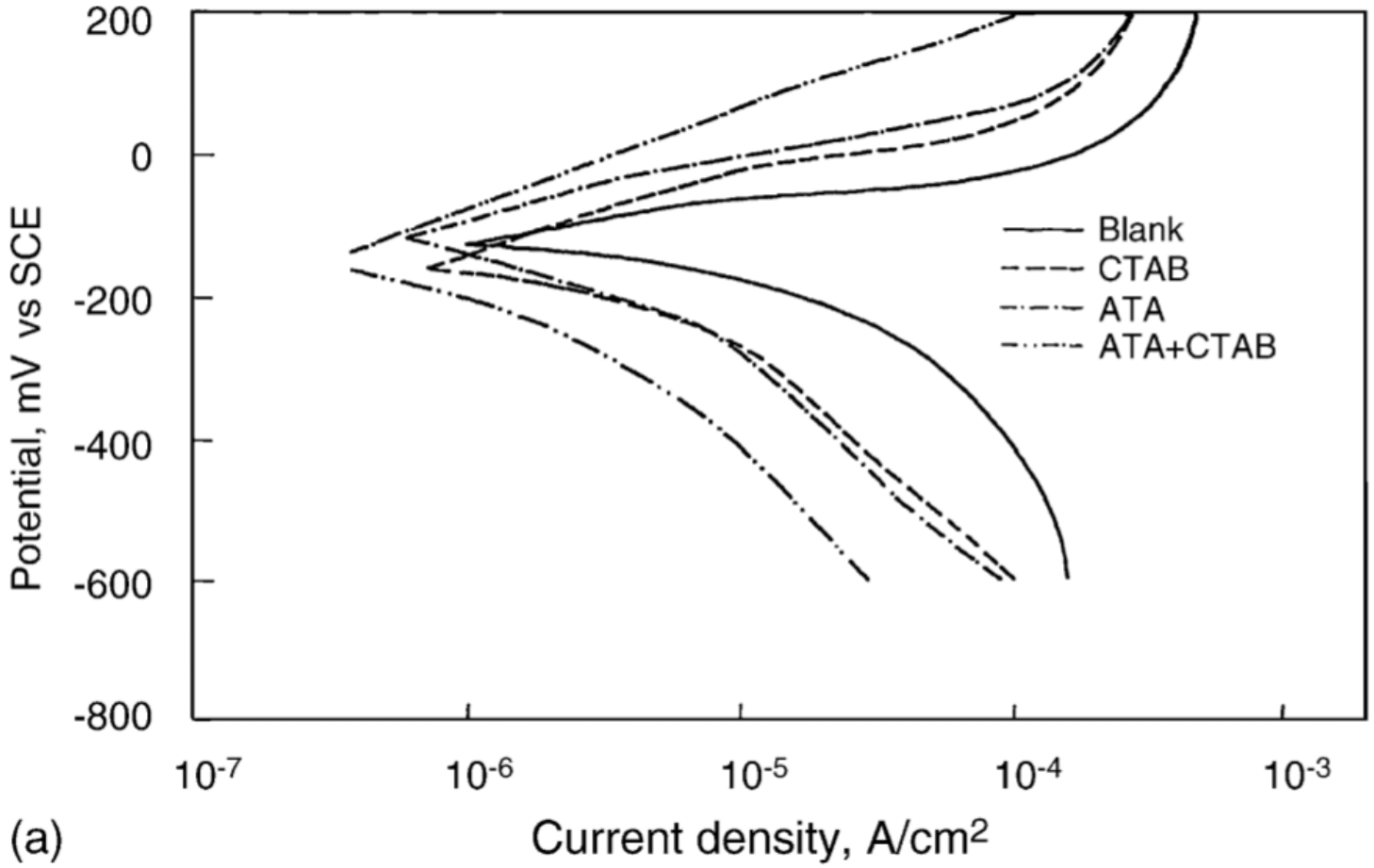
NH_3 in bicarbonate likely exists as NH_4^+

$NO + H_2O \rightarrow H_2NO_2$

Nitrous acid lowers pH, increases competitive H_2 evolution

SO_x likely has same effect

Ammonium as Cu Passivator

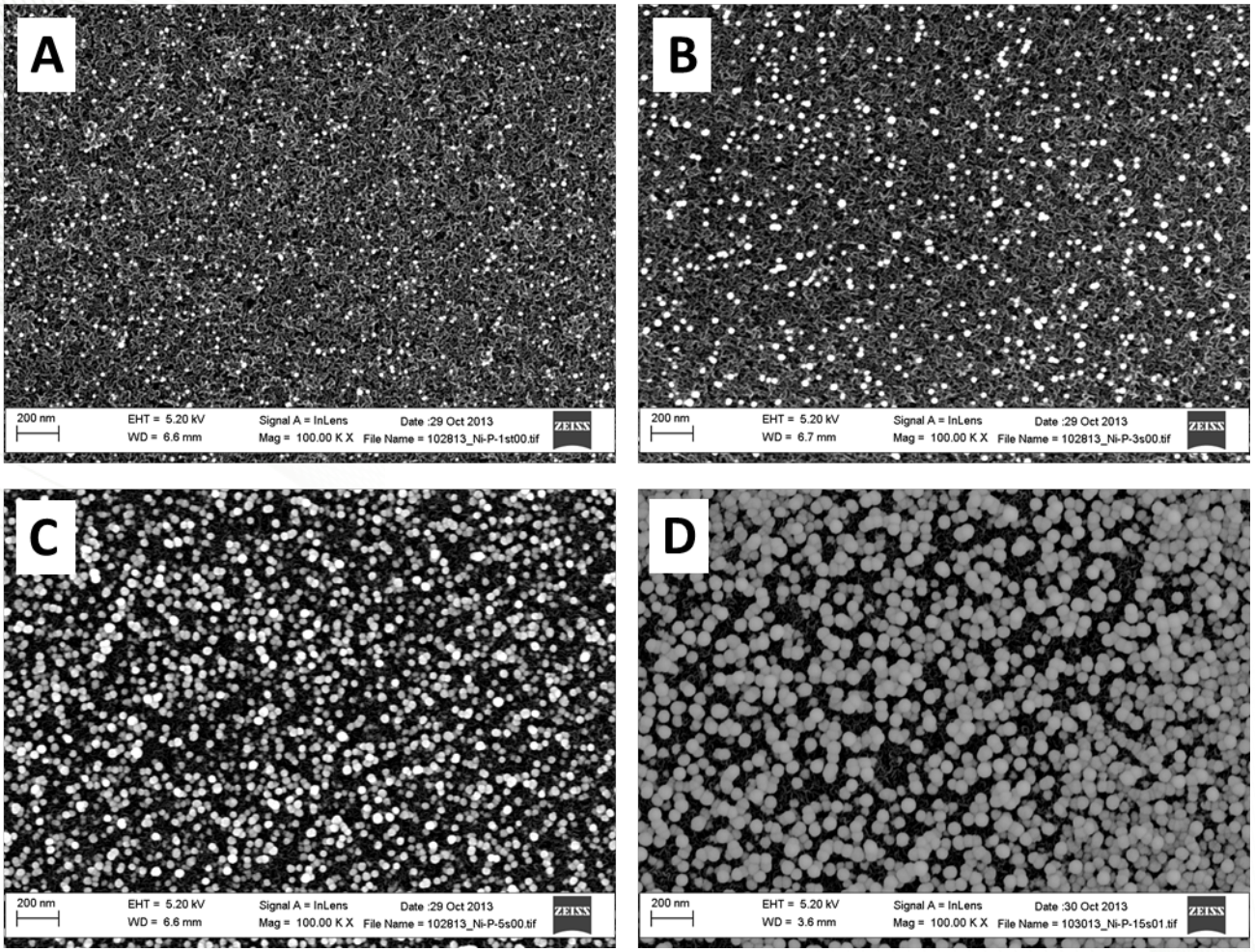


A. Lalitha et al. / Electrochimica Acta 51 (2005) 47–55

Summary for Contamination Tolerance

- Sulfur tends to foul the reaction
  - Not strong or immediate, but reduces to stable copper sulfides
  - Sulfur contamination is likely problematic for any Cu-based system
- Nitrogen species are strong inhibitors of the reaction
  - Due to tendency to reduce to ammonium
  - More specific to nanospike catalysis
- In both cases, can be mitigated by periodic dissolution and re-nucleation of copper co-catalyst

Electronucleation of Particles



Summary

- Have demonstrated that vapor phase operation is possible, but current density is still low
  - Can fabricate gas diffusion electrode using our nanospike catalyst
  - Electrode is stable
  - Reaction mechanism intact
  - Unresolved issues with hydration and separator membrane
- Have investigated the impact of coal combustion contaminants, primarily S and N species
  - Poisoning understood to occur at Cu nanoparticle
  - Sulfur somewhat tolerated
  - Nitrogen generally not tolerated
  - Mitigation possible through in-situ regeneration of Cu particles
  - All copper based catalysts could be subject to this poisoning effect

Acknowledgement

Acknowledgment: This material is based upon work supported by the Department of Energy under Field Work Proposal: #FEAA132.

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